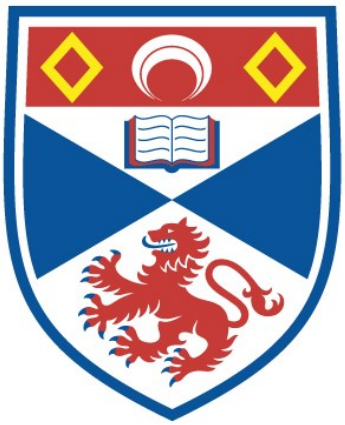
THE THERMAL REACTION OF TOLUENE AND IODINE AND SOME RELATED PROCESSES

William Alexander

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE THERMAL REACTION

OF

TOLUENE AND IODINE

AND SOME RELATED PROCESSES

being a Thesis

presented by

WILLIAM ALEXANDER B.Sc.

to the

UNIVERSITY OF ST. ANDREWS

in application for

the

DEGREE OF DOCTOR OF PHILOSOPHY

September 1957.

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DECLARATION

I hereby declare the following Thesis to be a record of the results of experiments carried out by me, and furthermore, that the Thesis is of my own composition, and has not been previously presented in application for a Higher Degree.

The investigations described were carried out in the Chemical Research Laboratories of St. Salvators College, St. Andrews, under the supervision of Dr. Charles Horrex.

UNIVERSITY CAREER

I entered the United College of the University of St. Andrews in October 1948, and graduated with First Class Honours in Chemistry in July, 1952.

The research described in this thesis was carried out in the United College under the direction of Dr. Charles Horrex within the period July 10th, 1952, to 20th September, 1955.

CERTIFICATE.

I hereby certify that Mr. William Alexander has spent twelve terms at research work under my direction, that he has fulfilled the condition of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. Charles Horrex for his invaluable assistance and advice in the practical and theoretical aspects of this investigation, to Dr. R.B. Cundall and Mr. R.N. Pittilo for many helpful discussions on the practical side of the investigation.

The author also wishes to thank Professor John Read, F.R.S., for the provision of facilities to carry out this research, and the Department of Scientific and Industrial Research for the award of a maintenance allowance.

INDEX.

	PAGE.
Introduction	1
Bond Energies Defined	2
Latent Heat of Sublimation of Carbon	6
Methods of Determining Bond Energies	6
Application of Thermochemical Data	14
Reaction of Atoms and Free Radicals with Molecules	15
Abstraction Reactions of Free Radicals	22
The Recombination of Radicals and Atoms	23
Previous Determinations of the (C - H) Bond Dissociation Energy in Toluene	26
The Mass Spectrometer	37
Apparatus and Experimental Technique	40
Circulation Pump	40
Rate of Flow Measurement	43
Purification of Carrier Gas	45
Temperature Control	47
Injector Units	49
Preparation and Purification of Reactants	55
Analysis of Products	58
Description of an Experiment	61
Reaction between Toluene and Iodine	61
Reaction between Dibenzyl and Iodine	69
Reaction between Dibenzyl and Hydrogen Iodide	78

DISCUSSION.	PAGE.
General Reaction Scheme	80
Secondary Processes in the Toluene-Iodine Reaction	85
Stability of Dibenzyl Radical	90
Thermodynamic Estimation of Equilibrium Possibilities in Reaction Systems	97
The System Dibenzyl and Hydrogen Iodide	101
The System Dibenzyl and Iodine	120
The System Toluene and Iodine	125
General Conclusions	132
Summary	133
Appendix (1)	136
(2)	137
(3)	138
(4)	139
(5)	140
(6)	144
(7)	146
References	147
Collected Tables of Results	150

SYMBOLS.

In Text.

$D(X - X)$	-	Dissociation Energy of Bond X - X.
$A(X^+)$	-	Appearance Potential of X.
$I(X^+)$	-	Ionisation Potential of X.
E_1	-	Energy of Activation of Process 1.
G^o	-	Standard Free Energy of the System.
H^o	-	Standard Heat Content of the System.
S^o	-	Standard Entropy of the System.
e.u.	-	Entropy Units - calories/degree.

In Tables.

(Tol)	-	Concentration of Toluene.
(Bz)	-	Concentration of Benzyl Radicals.
(DB)	-	Concentration of Dibenzyl.
(I_2)	-	Concentration of Molecular Iodine.
(I)	-	Concentration of Atomic Iodine.
(HI)	-	Concentration of Hydrogen Iodide.
K cals	-	1000 calories.

INTRODUCTION.

The work reported in this thesis arose from some observations made by R.B. Cundall[1] in the laboratories at St. Andrews while he was investigating the pyrolysis of methyl iodide. An attempt to use toluene as a radical acceptor resulted in the production of some hydrogen iodide, and Cundall attempted a brief investigation into its source. The reaction of iodine with toluene was suspected, and in some initial experiments, the reaction was investigated in a flow system.

In these experiments it was shown that stilbene and dibenzyl condensed out at the furnace exit, and that benzyl iodide, hydrogen iodide and unreacted toluene and iodine condensed out in the analysis traps.

The only other references to this reaction are recorded in Beilstein[2], where it is noted that the prolonged heating of toluene and iodine vapours together yields hydrogen iodide and other products. Other investigations have shown that the prolonged refluxing of toluene, to which iodine has been added, produced no hydrogen iodide.

The aim of the work described in this thesis was to investigate the products and kinetics of the reaction. It was hoped that additional data on the question of the bond strength of the side chain (C-H) link in toluene might be obtained since a study of the bromination of the latter had recently yielded a new value for this bond dissociation energy. The results quoted in later sections of this thesis on the reaction of toluene with iodine are explained by a primary reaction between the hydrocarbon and an atom of iodine. This step produces a benzyl radical and hydrogen iodide, and appears to be markedly inhibited by the addition of excess hydrogen iodide. The presence of dibenzyl and stilbene in the products rendered it

necessary to investigate the reaction of dibenzyl with iodine, and with hydrogen iodide. The results of these investigations are given in later sections.

Before dealing with the experimental work of this thesis, and discussing it, a brief survey is given of some relevant themes and studies reported in the literature, and which form a background against which this present investigation has to be considered.

BOND ENERGIES.

Some General Points.

Chemical reactions involve the rupture and formation of chemical bonds, and the rate at which these processes take place is often determined by the relative strengths of the bonds involved.

The bond energy concept has developed in three distinct phases. In the first phase, research was directed to assessing, rather approximately, the strengths of individual bonds in different molecules. The results tended to emphasise the constancy of bond energy values for a given link in different molecules, although anomalies did exist.

In the second period greater attention was paid to these anomalies, and Pauling[3] was able to explain them, and the variations in the strengths of like bonds in different molecules, by use of the quantum mechanical concept of resonance. It was also found possible, by making a rather large number of simplifying assumptions, to calculate theoretically the strengths of the simplest of bonds, :eg: H_2 and H_2^+, by the application of wave mechanics. Probably the greatest advance in this period was the general recognition of

the fact that individual bond strengths were not independent of their environment in the molecule.

Since then further advances in practical technique have yielded more accurate determinations of individual bond strengths. With the availability of these more accurate determinations, much thought has been given to finding out relationships between the variations in bond strengths and other properties of the molecule.

The more accurate values allow us to make deductions concerning the heats of formation of radicals and reaction intermediates. An accurate knowledge of bond strengths is useful also in other fields. The possibility of a chemical change occurring and the conditions of equilibrium can be predicted by the use of thermodynamic laws given the appropriate thermochemical data. However, we are unable to predict the reaction rate by the use of thermodynamics, nor are we able to discriminate between reaction paths. A precise knowledge of the strengths of the bonds involved in the process can assist us in predicting the path it will most probably follow.

Unfortunately, as the research work has grown in quality and quantity, so also have the number of definitions relating to bond strengths. The nomenclature used in discussing bond strengths often varies from author to author, and it will be appropriate to define the symbols, and terms, to be used in this thesis and discuss their relationship to one another.

BOND DISSOCIATION ENERGY. (D):- is defined as the endothermicity of the reaction in which a molecule dissociates into unexcited fragments by the rupture of a single bond.

:ie: $R_1 - R_2 = R_1 + R_2 - D(R_1 - R_2)$ K cals/mole.

Normally this process should take place at $0^{\circ}K$ in the gas phase, but generally the difference between the value of D at $25^{\circ}C$ and $0^{\circ}K$ is very small, only of the order of 3 -5 K cals/mole, and values at $25^{\circ}C$ are frequently quoted in the literature. Furthermore, the precise nature and energy states of the fragments must be specified. It is obvious for the above reaction that $D(R_1 - R_2)$ will only equal the true bond dissociation energy if the fragments R_1 and R_2 are in their ground states.

The bond dissociation energy takes into account the effect of molecular environment on the strength of a bond. As an example, some individual bond strengths are given below:-

$C_6H_5CH_2 - H$	77.5 (89)	K cals/mole.
$CH_3 - H$	101	K cals/mole.
$CMe_3 - H$	86 - 89	K cals/mole.

It is also to be noted that bond dissociation energies are in most cases directly determined, and are thus independent of any calculations involving the value of the latent heat of carbon.

AVERAGE BOND ENERGY. (q.):- was introduced by Fajans[4] on the basis of experimental observations that the heat of combustion and therefore the heats of formation of isomeric substances are almost the same; and the heats of formation of compounds forming a homologous series increase by equal increments for each methylene group added.

Recently, the average bond energy has been defined as the work required for the rupture of the bond in a process during which all the other bonds are independently, and simultaneously, extended in such a way that the molecule as a whole swells infinitely without losing its geometrical form. In the simplest cases, :eg: homobonded molecules of the type(XY_n), containing n bonds, all identical, we have from the above definition the average bond energy, q(X-Y), given by :-

$$q(X\text{-}Y) = 1/n\ Q_f^a\ (XY_n).$$

where Q_f^a is the heat of formation of the gaseous compound from its gaseous constituent atoms in their standard states.

Thus for methane:-

$$q(C\text{-}H) = 1/4\ Q_f^a\ (CH_4).$$

The average value of the (C - H) bond energy obtained in this way is assumed valid for calculations involving heterobonded molecules :eg:- for the (C-C) bond in ethane,

$$q(C\text{-}C) = Q_f^a\ (C_2H_6) - 6q(C\text{-}H).$$

By the use of this method Pauling[3] and others have drawn up tables of average bond energies derived from thermochemical data. For the average (C-H) bond energy in methane, Pauling derives a value, q (C-H) = 87.3 K cals/mole, by assuming the latent heat of sublimation of carbon L_c = 124.3 K cals/grm atom

:eg: C diamond = C_g - 124.3 K cals/grm atom = $C_g - L_c$.

The absolute value of any average bond energy involving carbon is dependent on the particular value of the latent heat of sublimation chosen.

Latent Heat of Sublimation of Carbon.

The latent heat of sublimation of carbon has long been the subject of much dispute. Springall,[5] in a comprehensive review of the literature up to 1950, indicated that there were four main possibilities which he arranged in the following order of probability:- 136, 141, 170.4, 125.0, K.cals/grm atom.

Since 1950 a large number of independent investigations have been carried out mainly using mass spectrometer techniques.[6] In spite of this additional research, the absolute value of the latent heat of carbon is still uncertain. At the present it would seem that the most probable value for L_c is 141.0 K.cals/grm atom at $0^{\circ}K$. From the point of view of chemical kinetics, the bond dissociation energy is more important although a knowledge of average bond energies is helpful in the assessment of resonance energies.

Methods of Determining Bond Dissociation Energies.

This subject has been excellently reviewed by Szwarc[7] and therefore only those methods which have been associated with the determination of the bond energies of bonds of the type ($PhCH_2$-X) will be considered in detail.

Bond Splitting Processes.

a. Spectroscopic.

For the determination of bond dissociation energies the details of the pure vibrational spectrum would be the most useful data. The onset of continuous absorption at a frequency ν can give a value $D = Nh\nu$, (where N = Avogadros number and h = Planck's constant), which corresponds to a dissociation process. The process may however produce one of the

products in an excited state and the value of D has to be interpreted with this complication.

The spectra of molecules containing a large number of bonds are very complex indeed, and the method is generally limited to diatomic molecules. Even so, it is frequently impossible to discern the convergence limit and reliance has to be placed on extrapolation techniques. The most common method of graphical extrapolation used is due to Birge and Sponer,[8] and involves plotting ΔE, (energy difference between two successive vibrational levels) against the vibrational quantum number. On extrapolation, the area under the curve gives the bond dissociation energy. The accuracy of the method depends on the sufficiency of the data available.

ELECTRON IMPACT. This method has been used successfully by D.P.Stevenson and others,[9] and consists of bombarding gaseous molecules of the compound (inside a mass spectrometer source) with electrons of known energy. As the average energy of the bombarding electrons is slowly increased, a point will be reached where the impact of the collision produces the process,

$$RX \longrightarrow R^+ + X + e \text{ ----------(1)}$$

The electron accelerating potential at which this occurs is called the Appearance Potential (A^+).

If the energy for the change $R \longrightarrow R^+ + e$ -- (2) is known then the bond dissociation energy for the process :-

$$RX \longrightarrow R + X$$

can readily be calculated. Unfortunately the method is not so simple as it appears. Due to the spread of the ionising electron energies,

the ion current is not a linear function of the accelerating electron voltage over the entire range, and instead of intersecting the electron voltage axis, it curves exponentially towards it at low ion currents.

Various methods have been proposed for the interpretation of this initial curvature, and the relative merits of each have been discussed by Morrison.[10] In normal practice, the ionisation curve for argon (the ionisation potential of argon has been determined spectroscopically), is plotted simultaneously with that of the ion under investigation, and the ionisation potential so obtained is corrected for any discrimination effects due to the instrument.

Recently, methods have been developed by which the initial K.E. of the ion can be estimated and allowed for. This method of determining bond dissociation energy is likely to prove very useful in determining the bond strengths in radicals.

Franklin and Fields[11] have recently published an interesting article on the effect of ring substitution on the appearance potential of the benzyl ion. Comparison of the experimental values with theoretical showed that substitution in the ring did not alter the appearance potential of the benzyl ion. Furthermore, tolyl ions produced by electron impact instantly rearrange to the corresponding benzyl isomers. This latter claim is interesting in view of the later work by Lossing[12] and collaborators who claimed to measure the statistical ratio of tolyl to benzyl ions by the use of tri-deutero toluene. Lossing has also pointed out that although the appearance potential of the benzyl ion as determined by electron impact on toluene yields an α (C - H) bond dissociation energy

which agrees well with that obtained by Szwarc[13] in pyrolytic studies, the use of this value of A. ($B\dot{z}^+$), together with that obtained for the same ion from studies of dibenzyl itself, to calculate I^+ ($B\dot{z}^+$), does not give a value in agreement with I^+ ($B\dot{z}^+$) as determined by investigations on benzyl iodide. From this, Lossing concludes that at present this method cannot be used to confirm Szwarc's value of 77.5 K cals/molesfor D(C-H) in toluene.

THERMAL METHODS.

a) Equilibrium method depends on the attainment of complete thermodynamic equilibrium at various temperatures between the parent substance and its dissociated fragments, : eg:

$$R\text{-}R' \longrightarrow R\text{-} + R'\text{-}$$

This method cannot be applied to substances which dissociate to give fragments which will react with the parent substance and, consequently, has had limited application to the dissociation of compounds into free radicals. However, Preckel[14] has determined the bond dissociation energy for the dissociation of hexa aryl ethanes into comparatively stable radicals.

The most useful application of this method has been the determination of the dissociation energies of the halogens.[15] Probably the most accurate determination is due to Perlman and Rollefson[16], who introduced many refinements in technique and calculated D(I-I) = 35.514 $\pm$ .05 K cals in excellent agreement with spectroscopic data. More recently this method has been applied with great success to estimating the bond dissociation energy in the fluorine molecule.

In a recent investigation Benson[9] has measured the equilibrium between toluene, bromine, benzyl bromide and hydrogen bromide and used the value of the equilibrium constant, together with the entropy of the benzyl bromide estimated from spectroscopic and other data to determine the value of ΔH^{o} for the equilibrium. This value together with the heat of formation of benzyl bromide yields a value for the α(C-H) bond energy in toluene of approximately 84 K cal/mole.

b) Chemical Kinetic Method.

Chemical Kinetics deals with the mechanism of chemical reactions and the rates at which they occur. Suitable analysis of these changes yields an energy factor, defined as the Energy of Activation, E_a, which is a function of the bond(s) broken and the bond(s) formed.

In order to apply chemical kinetics to the determination of any single bond dissociation energy, the relation between the activation energy for the process and the bond dissociation energy must be known. In the simplest case, the dissociation :-

$$R\text{-}R' \longrightarrow R\text{-} + R'\text{-} ,$$

the unimolecular rate constant is defined as;

$$k = 2.303/t \; \mathrm{Log}_{10} a/(a - x).$$

where t is normally in seconds, a is the initial concentration, and (a - x) is the concentration of RR' at time t. Evaluation of k for a series of temperatures permits the activation energy of the reaction to be found by means of the Arrhenius expression;

$$\mathrm{Log}_{10} k = \mathrm{Log}_{10} A - E_a/4.57 \; T$$

the energy of activation of the process being equivalent to the bond

dissociation energy in question only if the following conditions are satisfied.

1) Any back reaction should have zero activation energy ie:

ΔH for the reaction = E_a forward reaction, = bond dissociation energy.

2) The bond dissociation in question should be the rate determining step of the reaction with rate constant k.

In order that (2) can be asserted with confidence it is necessary that

3) The mechanism should be clearly established.

4) Side reactions should be repressed or their extent known accurately.

In much of the earlier work little or no investigation was carried out into the products of the reaction, and hence mechanisms were more or less guessed. Many of the original 'true' first order reactions have since been shown to proceed by chain mechanisms. Most of the early data were derived from investigations carried out in static systems with high pressures of reactants, and consequently greater opportunities for side reactions. Modern experimental methods have developed techniques to minimise side reactions by the use of low pressures of reactants, and the addition of radical acceptors to minimise secondary reactions between the reactant and its dissociation products.

The earliest work along these lines was performed by Paneth and Hofeditz,[17] and by Rice,[18] who introduced metallic mirrors to remove the radicals produced by the pyrolysis of organic compounds. This method has been used to determine reaction rates and bond dissociation energy values but Szwarc[19] has pointed out that the method is liable to inaccuracies due to the failure to destroy the radicals at the moment of their formation in the hot zone of the furnace.

Polanyi,[20] using a flow system which permitted very low pressures of

reactants and small contact times, superficially investigated the decomposition of a large number of iodides. In his work it was assumed that the secondary reactions between R- , I , and RI, were negligible, and the values for the various bond dissociation energies which he obtained are remarkably consistent with more modern determinations.

A further interesting development in this field has been the introduction of toluene as a carrier gas and radical acceptor, making use of the fact that benzyl radicals are thermally stable and unreactive as shown in the work of Szwarc and Horrex.[21] In general, the more reactive species of the radicals formed react with the toluene to produce benzyl radicals. eg:

$$R- + C_6H_5\ CH_3 = RH + C_6H_5CH_2-$$

The benzyl radicals survive the short contact time in the hot zone and dimerise to form dibenzyl. By this simple method both back and chain reactions can be effectively prevented, and the initial rate of dissociation can be estimated from the rate of formation of RH or of dibenzyl. This method can only be used to determine bond dissociation energies which are weaker than the α(C - H) bond dissociation energy in toluene, (otherwise the pyrolysis of toluene itself would considerably complicate matters,) and it has been most applied to the determination of the bond dissociation energies in substituted benzyl derivatives. Many examples of its use are now available in the literature.[22]

In several cases the unimolecular fission of the bond has been the rate determining factor and the kinetics of the decomposition have thus been greatly simplified. An example[23] of such a reaction is the pyrolysis of benzyl bromide in which,

$$C_6H_5CH_2Br \rightarrow C_6H_5CH_2 - + Br -$$

is the rate determining step.

Likewise Szwarc[24] has postulated that the rate determining step in the pyrolysis of toluene is;

$$C_6H_5CH_3 \longrightarrow H + C_6H_5CH_2 -$$

followed by

$$C_6H_5CH_3 + H \rightarrow C_6H_5CH_2 - + H_2$$

or

$$C_6H_5CH_3 + H \rightarrow C_6H_6 + CH_3 -$$

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 -$$

finally $PhCH_2 - + PhCH_2 - \longrightarrow$ Dibenzyl

However, Steacie[25] in a later investigation showed

a) the presence of diphenyls,

b) the amount of dibenzyl formed was much less than that expected with Szwarc's mechanism,

c) the mechanism for the formation of methane and benzene was not well established,

d) Relatively large quantities of hydrogen were formed in the pyrolysis, which could only be explained by the presence of dibenzyl in the reaction zone. In view of these major complications in the kinetics, it was thought premature to assign a value to the (C - H) bond dissociation energy in toluene.

It may be pointed out that these conclusions render Szwarc's results open to doubt.

APPLICATION OF THERMOCHEMICAL DATA TO THE ESTIMATION OF BOND DISSOCIATION ENERGIES.

If sufficiently accurate thermochemical data are available, then a whole series of bond dissociation energies may be derived from one measured value. Consider the reaction; -

$$RX + Y = RY + X + Qs.$$

where Qs is the heat of substitution; then, $Qs = D(R-Y) - D(R-X) = Qf(RY) - Qf(RX) + Qf(X) - Qf(Y)$, where $Qf(RX)$, etc. are the heats of formation of gaseous RX, RY, X, Y, from their elements in their standard states. Hence the value for D(R-X) can be obtained if D(R-Y) is known.

This method of calculating additional bond energies has been more often applied in free radical studies in the following manner.

Consider the reaction; -

$$RX = R- + -X. \quad \text{where X is a halogen atom}$$

$$D(R-X) = Qf(RX) - Qf(R) - Qf(X).$$

If D(R-X) is obtained experimentally from kinetic studies then the heat of formation of the radical R- can be calculated. Using this value, and provided appropriate thermochemical heats of formation are available, the bond dissociation energy of any compound formed by the condensation of R- with any other atom or radical may be estimated. An application of this method to the calculation of $D\alpha(C-H)$ in toluene using the experimentally derived value for D(Bz-Bz) will be given later. ($Bz_{\alpha} = C_6H_5CH_2$ -).

THE REACTIONS OF ATOMS AND FREE RADICALS WITH MOLECULES.

The reaction scheme proposed at a later stage, (See Discussion) involves examples of the attack of molecules by free atoms, (:eg: I atoms on toluene or dibenzyl), and by free radicals. (Bz+ III). It is therefore relevant to examine the present state of knowledge in related fields. Unfortunately the free atoms which have been studied most often are, Na, H, Cl, Br, and very seldom has much work been done on metathetical reactions involving Iodine atoms. In the radical field however, the reactions of alkyl radicals have been extensively investigated, but the benzyl radical has most often been treated as if it were quite stable and unreactive. Thus work of a strictly comparable nature to the subject under investigation is not available.

The suggestion that free atoms can play a part in reaction mechanisms dates from the introduction of ideas of quantum yields into photochemistry. Subsequently, the direct investigations of atomic reactions were given a great impetus by the work of Polanyi[26] on the reaction of alkali metal atoms with various halides. The important factors for the purpose of this thesis, are the magnitudes of the rate constants and the temperature coefficients of the various reactions which give the energies of activation.

The early work of Bodenstein,[27] followed by that of Polanyi, established that the true activation energies of many atomic reactions, (after allowance for any unavoidable endothermicity of a process), were low. This is illustrated by the following data obtained by Polanyi's techniques:-

TABLE 1.

Reaction- Na + R-X ⟶ NaX + R-

Na	+	CCl_4	⟶	NaCl	+	CCl_3 -	E_a = 0	K cals/Mole
Na	+	CF_3I	⟶	NaI	+	CF_3 -	E_a = 1.8	" "
Na	+	CF_3Cl	⟶	NaCl	+	CF_3 -	E_a = 7.0	" "
Na	+	$CHBr_3$	⟶	NaBr	+	$CHBr_2$ -	E_a = 0.3	" "
Na	+	$CHCl_2Br$	⟶	$CHCl_2$-	+	NaBr	E_a = 1.5	" "

A variety of studies have been made of the reactions of H, Cl, and Br atoms and again the true energies of activation appear to be quite low.

REACTIONS INVOLVING H ATOMS.

One basic difficulty in reactions involving hydrogen atoms has been the measurement of the concentration of the free atoms. Due to the uncertainty in the value of the latter, much of the earlier work using discharge tubes as the source of free atoms did not determine temperature coefficients of reaction, but calculated the collision yield of the reactions, and deduced energies of activation. A few such energies of activation are given below.

TABLE 2.

Reactions of Type H + RH = H_2 + R-.

Hydrocarbon	Coll. Yield x 10^7.	Ea K cals	Ref
Propane	.46	8.6	28
Cyclopropane	.11	9.5	28
2-Methylpropane	.24	9.3	29
22-Methylpropane	.17	9.2	30

More recent work has used a method of comparing the required reaction rate for D atoms, with that for a standard process. Darwent and Roberts[31] produced deuterium atoms by the photolysis of D_2S, and compared the temperature dependence, and reaction rate for the formation of D_2 due to the reaction, $D + D_2S = D_2 + DS$, with the corresponding quantities for the process $D + H_2 = HD + H$, simultaneously obtained when the photolysis system contained a mixture of D_2S and H_2. The constants for the first reaction were deduced by assuming Farkas and Farkas's[32] data for the second. The process was then repeated for mixtures of D_2S with a hydrocarbon when the further reaction occurred:-

$$D + RH = HD + R-.$$

By this means the following values of Ea and A were obtained for the reaction between deuterium atoms and hydrocarbon molecules.

TABLE 3.

Reactions of the type, $D + RH = HD + R-$. [31,33]

Hydrocarbon.	Ea. K cals.	log A mole^{-1} litre sec^{-1}
Ethane	9.0	11.4
Propane	7.2	11.5
2- Methylpropane	6.3	11.5
Propylene	5.0	10.7

An attempt has been made recently[34] to measure H atom concentrations by observation of the heat evolved on a platinum filament placed in a stream of hydrogen containing free H atoms. This method has so far been applied to the reaction of H atoms with methane and ethane. In both cases, the frequency factors and activation energies obtained appear to be rather low.

REACTIONS INVOLVING CHLORINE ATOMS.

The most investigated case is undoubtedly the reaction of chlorine atoms with hydrogen in the thermal and photochemical formation of HCl. The high quantum yields, (in favourable cases 10^6), and the behaviour in the presence of inhibitors, lead to the formulation[35] of the well known chain mechanism:-

$$Cl + H_2 = HCl + H \quad - \quad - \quad - \quad (a)$$

$$H + Cl_2 = HCl + Cl. \quad - \quad - \quad - \quad (b)$$

The individual reactions above have been studied by discharge tube and other techniques, and the values quoted for these very rapid reactions are:-

(a) $k = 10^{11.4} \exp(-6100/RT)$[36] (b) $k = 10^{11.4} \exp(-4700/RT)$[37]

Since the bond strengths D(H-Cl), D(H-H), and D(Cl-Cl) are approximately 103, 102, and 58 K cals respectively, process (b) is exothermic and (a) nearly thermoneutral. The high reaction rates, and small energies of activation are therefore not surprising.

Abstraction reactions with hydrocarbons, (RH), also show chain character and a close similarity to the above. This is not surprising since D(R-H) is of the order of 100 K cals for paraffin hydrocarbons. Thus the process,

$$Cl + R\text{-}H = R\text{-} + H\text{-}Cl$$

is approximately thermoneutral, while the next stage is exothermic. :eg:

$$R\text{-} + Cl_2 = R\text{-}Cl + Cl + 23 \text{ K cals.}$$

Few detailed investigations of the individual steps have been undertaken but the results available suggest the following generalisation. Steiner and Watson[38] have shown that the ease of abstraction in hydrocarbons varies in the sequence, tert-H>sec-H>primary H, i.e. in the order of increasing bond strengths. Trotman - Dickenson, Pike, and Pritchard[39] have investigated the attack of chlorine atoms on a gaseous mixture consisting of the hydrocarbon under investigation and hydrogen. The principle is the same as that used by Darwent and Roberts in their studies on deuterium atom reactions. The rate constants for the attack of Cl atoms on the hydrocarbons listed below, (Table 4) were obtained by comparing the rates of formation of HCl and RCl, and assuming that $k_c = 10^{10.9} \exp(-5500/RT)$ for the process;-

$$Cl + H_2 = HCl + H.$$

TABLE 4. (40)

Compound	Log A_{-1} mole^{-1} litre sec^{-1}.	Ea Kcals.
Ethane	11.1	1.0
2-Methylpropane	11.3	0.9
22-Dimethylpropane	11.1	0.7

REACTIONS INVOLVING BROMINE ATOMS.

The data available for reactions involving bromine atoms is in many ways more extensive and accurate than for the comparable reactions with chlorine atoms. This is really a reflection of the influence of bond strengths in determining chain lengths. It can readily be shown from thermochemical data that the corresponding chain propagating processes; -

$$Br + H_2 = HBr + H \quad -14 \text{ Kcals.}$$
$$Br + R\text{-}H = HBr + R\text{-} \quad -14 \text{ Kcals.}$$

are endothermic. These, therefore, become the rate determining steps in the

formation of HBr and RBr respectively. Consequently in the thermal reaction between bromine atoms and hydrogen, or hydrocarbons, a state of equilibrium is attained between the bromine atoms and molecules in the system. The reactions are much slower and the chain lengths shorter.

The reaction between bromine and hydrogen was investigated by Bodenstein and Lind,[27] who suggested that the rate of formation of HBr could be expressed by the following experimentally derived rate law:

$$d(HBr)/dt = 4k(H_2)(Br_2)^{\frac{1}{2}} / (10 + (HBr)/(Br_2)).$$

To account for this complex expression, the following mechanism was simultaneously proposed by Christiansen, Herzfeld, and Polanyi;[41]

$$Br_2 = Br + Br. \quad \ldots\ldots\ldots\ldots(2)$$
$$Br + H_2 \rightleftharpoons HBr + H \quad \ldots\ldots\ldots(3)$$
$$H + Br_2 \rightleftharpoons HBr + Br. \quad \ldots\ldots\ldots(4)$$

Analysis on the assumption of steady state kinetics yields the identical expression

$$d(HBr)/dt = K'(H_2)\,(Br_2)^{\frac{1}{2}} / (K'' + (HBr)/(Br_2)).$$

where $K' = 4k = 2k_3k_4/k_{-3}\,K^{\frac{1}{2}}$ and $K'' = 10 = k_4/k_{-3}$.

An analogous equation has been found to hold for the reaction between bromine and methane[42] and has been assumed to hold for various other hydrocarbon brominations. These investigations have provided the following data for the velocity constants.

TABLE 5.

Reactions of the type, Br + RH = HBr + R-.

RH	Ea Kcals	Log A mole^{-1} litre sec^{-1}	Ref
H_2	17.7	10.8	(43)
Ethane	13.9	—	(44)
2-Methylpropane	11.7	14.6	(45)
Toluene	7.6	10.5	(46)

REACTIONS OF IODINE ATOMS

The literature provides no reactions of the type ,

$$I + R\text{-}H \longrightarrow R\text{-} + HI.$$

presumably because the usual paraffinic R-H bonds are of the order of 94 - 103 Kcals in strength and this makes such reactions 23-32 Kcals endothermic. The subsequent process, R- + I_2 = R-I + I, would be exothermic and occurs readily, since it is well known that iodine has been used as a radical acceptor at low temperatures.

Several reactions are known where iodine appears to act as a catalyst, and in some cases a rate law involving $(I_2)^{\frac{1}{2}}$ has been established, eg: the decomposition of n-propyl,[47] iso-butyl,[48] and sec butyl iodides,[49] di-iodoethane,[50] diiodopropane,[51] and chloral.[52] The precise mechanism of such a catalytic action is not known, but the various explanations which have been put forward in these cases suggest the abstraction of a hydrogen atom from the decomposing substance to form HI, or the removal of I to form with the catalyst a molecule of iodine. It would seem reasonable to assume that for compounds with a weak R-H bond such as toluene, an abstraction of an α-hydrogen atom should be possible.

ABSTRACTION REACTIONS OF FREE RADICALS.

Reactions by which free radicals abstract hydrogen atoms from saturated molecules have been postulated from the earliest days of free radical chemistry. Rice[53] explained the nature of the thermal decomposition products of hydrocarbons by making abundant use of reactions of the pattern; -

$$CH_3\text{-} + R\text{-}H = CH_4 + R\text{-}.$$

The Rice-Herzfeld scheme for the kinetics of these decompositions is also well known.

The precise study of the individual steps in these reactions has only started in recent years. A major trouble causing the delay has been the determination of radical concentrations in reaction systems. It is not possible to get a thermal equilibrium between methyl radicals and ethane analogous to the equilibrium attained between bromine atoms and bromine molecules, and the studies which have been in progress in recent years have made use of the comparative method. If methyl radicals are produced in the presence of hydrocarbon RH, the abstraction reaction to form CH_4 occurs parallel to the dimerisation to give ethane. The comparison of the rates of formation of methane and ethane relates the two processes, and by assuming Gomer and Kistiakowski's[54] value for the rate of dimerisation of methyl radicals, the corresponding temperature coefficient and frequency factor for the abstraction reaction may be deduced.

Using this technique, the rate constants have been obtained for abstraction reactions involving methyl radicals with a large number of hydrocarbons. A few temperature independent factors and energies of activation are quoted below: (Table 6).

TABLE 6.

Metathetical Reactions of Methyl Radicals.

Reactant.	Ea. Kcals.	$\log_{10}$ A. mol L sec $^{-1}$.	Ref
Hydrogen	9.9	8.5	55
	15.3	11.8	56
Methane	14.3	8.5	57
Ethane	10.4	8.3	58
Butane	8.3	8.0	58
2-Methylpropane	7.6	8.0	58

The activation energy of the abstraction reaction would seem to vary directly with the strength of the bond attacked, and is quite small. The experimental frequency factors are much smaller than would be expected from collision theory, and are low for bimolecular processes. No investigations of this character are available on the reactions of benzyl radicals, but Pittilo[59] has established that benzyl radicals attack fluorene, and dibenzyl, to form toluene.

THE RECOMBINATION OF RADICALS AND ATOMS.

RADICALS Many radical recombination reactions are known, but few of the rate constants have been measured. The main trouble, as in the corresponding abstraction reactions, was the determination of the radical concentrations.

As previously noted, the rotating sector technique developed by Melville and Burnett[60] was applied by Gomer[54] to determine the average life time of methyl radicals produced by the photolysis of acetone. The velocity constant, $k_d = 10^{10.6} \exp(-0 \pm 700/RT)$ litre mol^{-1}sec^{-1} so derived has been confirmed by using a mass spectrometer[61] to measure the concentrations of methyl radicals and ethane.

The recombination of ethyl radicals[62] produced by the photolysis of diethyl mercury has also been investigated using the sector method, and although the reaction was somewhat complicated, the energy of activation and frequency factors are of the same order as that obtained for methyl radicals.

No investigations have been undertaken to determine the rate of dimerisation of the higher alkyl radicals possibly because of difficulties due to the disproportionation of the radicals themselves. No such investigation has been carried out on the relatively stable benzyl radical.

TABLE 7.

Recombination of free radicals

Radicals	Ea.Kcals	Log A mol^{-1} litre sec^{-1}.
Me + Me	0	10.7
Et + Et	<.7	10.3

RECOMBINATION OF ATOMS.

Two methods have been used to investigate the rate of recombination of halogen atoms in the presence of inert gases, and in both cases, the investigations have been confined to the recombination of bromine and iodine atoms.

In method 1 a static system is used, the iodine and inert gas are admitted at pressures of 0.15 and greater than 100 mm respectively, and the percentage dissociation, which is small under these conditions, is measured by means of a double beam balanced photocell circuit. Rabinowitch and Wood[64] showed in an extensive investigation that the rate of recombination of iodine atoms in a static system obeyed the following rate law:-

$$-d(I)/dt = k(M)(I)^2.$$

Furthermore different inert gases possessed different efficiencies in promoting the recombination, the efficiency rising with the complexity of the inert gas molecule.:eg: the relative efficiencies of benzene and helium in the recombination of iodine atoms are, 175:3.4. Evidence was also established that the recombination reaction possessed a negative temperature coefficient for all inert gases, yielding an activation energy of -2 Kcals/mol.

Method 2. Flash photolysis technique.

The great disadvantage of method one is the very small percentage dissociation obtained. So far, no steady light source has been developed which will increase the absorption, and hence the percentage dissociation. The dynamic study of atomic recombinations has become possible with the advent of high intensity flash tubes, with which large concentrations of atoms (ca 20% dissociation) can be transitorily produced. The flash itself is of the order of 1 millisecond and the reaction is complete in approximately 20 milliseconds. The change in light intensity is amplified by means of a photomultiplier tube and conventional amplifier, and is recorded by photographing the trace produced on the screen of a synchronised oscillograph. The results[63,65] obtained by this method agree within the limits of experimental error with those obtained by method 1.

A further method developed to measure the rate of recombination of bromine atoms consists of comparing the thermal and photochemical rates of bromination in organic reactions, The results deduced by Ritchie[66] agree with those of Rabinowitch and Wood, but other applications of this method have not been so successful.

From the above investigations it would appear that the energies of activation in atom and radical recombinations are extremely small, and in

the case of free radicals the frequency factors are also quite low. The whole field of atom and free radical reactions, and energy transfer, has recently been reviewed by Trotman-Dickenson.[40]

RECENT INVESTIGATIONS UNDERTAKEN WITH A VIEW TO DETERMINING DIRECTLY OR INDIRECTLY THE (C-H) BOND DISSOCIATION ENERGY IN TOLUENE.

DIRECT METHODS

a) The pyrolytic decomposition of toluene.

Previous to 1948 the direct pyrolysis of toluene had only been conducted under conditions which rendered the derivation of a reaction mechanism almost impossible. Tilicheev[67] had shown that the pyrolysis of toluene in the presence of various catalysts proceeded at a rate thirteen times faster than benzene. He suggested that the energy of activation for the decomposition would be in the region of 70 Kcals/mole. Jost and Muffling[68] measured the rate of pyrolysis of toluene in a static system, following the course of the reaction by the increase in pressure. They observed that the reaction rate was unaffected by the presence of $Hg(Me)_2$ and therefore concluded that the decomposition was not a chain reaction.

Hein and Mesée[69] investigated the pyrolysis of toluene in the presence of Hg vapour, but were unable to determine an energy of activation from their results.

In 1948 Szwarc[71] reinvestigated the pyrolysis using a flow technique. The investigations were carried out over the temperature range 680-850°C, under a pressure of 2-15mm Hg, and with contact times adjusted to produce .01 - 1.25% decomposition. It was found that the reaction rate was independent of contact time, (four fold variation .2-.9 sec.) surface to volume ratio, (varied 15x.) and partial pressure of toluene. The products were identified as undecomposed

toluene, methane, hydrogen, benzene and dibenzyl, plus traces of other compounds which were not defined. The hydrogen to methane ratio was estimated by passage through a CuO cell, and confirmed by total combustion in oxygen followed by estimation of the CO_2 formed. The pyrolysis produced only two gases, H_2 and CH_4 in the constant proportion 60% H_2 to 40% CH_4, No C_2 gases were observed.

For a limited number of runs the quantity of dibenzyl was estimated by weighing, although no reference is made as to how it was separated from the diphenyls. The results were examined in terms of a first order constant k and the Arrhenius plot log k v $1/T^{o}A$ gave a straight line of slope corresponding to an activation energy of 77.5 Kcals/mole and a frequency factor of 2×10^{13}. This confirmed the view that the reaction was homogeneous and first order and the following mechanism was postulated for the decomposition; -

$$C_7H_8 \rightarrow C_7H_7^{-} + H \quad \ldots\ldots\ldots(1) \text{ (rate determining step.)}$$

followed by $$H + C_7H_8 \rightarrow H_2 + C_7H_7^{-} \quad \ldots\ldots(2)$$

and $$2C_7H_7^{-} \rightarrow Ph.CH_2.CH_2.Ph \quad \ldots\ldots\ldots(3)$$

The presence of methane and benzene was explained by the following reactions;-

$$H + C_7H_8 \rightarrow C_6H_6 + {}^{-}CH_3 \quad \ldots\ldots\ldots(4)$$

$$CH_3 + C_7H_8 \rightarrow CH_4 + {}^{-}C_7H_7 \quad \ldots\ldots\ldots(5)$$

The mechanism accounted for the observed products, (H_2 , CH_4 , C_6H_6, and dibenzyl.) and gave the correct proportions of products, 1 mole dibenzyl to 1 mole of gas produced. No further reference was made to the claim that diphenyls were produced, nor was any mechanism suggested to account for their production. The value 77.5 Kcals/mole was identified with the energy required to rupture the α(C-H) bond in toluene.

Making use of Stevenson's[70] value D(C-H) = 102 Kcals/mole for the rupture of the first bond in the methane molecule, the resonance energy of the benzyl radical was computed to be 24.5 Kcals/mole and its heat of formation = 37.5 Kcals/mole. This value for the resonance energy was identical with that deduced by Szwarc[71] from other data and seemed to confirm the accuracy of the above deductions.

The reaction was reinvestigated by Steacie[72] and his collaborators who disagreed with many of the results observed above. The pyrolysis was conducted in a flow apparatus very similar to that used by Szwarc in his investigation. A sharp separation of the volatile products was attained by use of a high efficiency vacuum still, and the residual non volatile material was estimated by weighing. The methane hydrogen ratio was measured initially by means of a mass spectrometer, but subsequently the more accurate combustion analysis was used. These methods showed that the quantity of hydrogen produced was 69% and not 60% of the noncondensible fraction, although the results agreed with those of Szwarc in that the ratio was independent of the reaction parameters such as temperature and contact time.

The volatile fraction was shown to consist of styrene, in addition to the benzene observed by Szwarc. The non volatile residue was separated into several fractions by chromatographic analysis, and the presence of methyl-diphenyls amply demonstrated. After the dibenzyl had been characterised by its infra red spectrum, it was concluded that dibenzyl may have made up less than half of the involatile material.

The rate studies, (based on the sum of the H_2 and CH_4 formed), showed a definite variation in k with contact time.(a sixfold variation in contact time induced a threefold variation in k.) The rate constant was also

found to vary with pressure and the condition of the surface of the reaction vessel. Furthermore, a plot of the log of the first order rate constants v $1/T^{\circ}A$ indicated an activation energy in the region of 90 Kcals/mole, although this energy was not ascribed to any one reaction step.

Further investigations were pursued by these authors into the formation of dimethyl diphenyl and, in an appendix to the paper, it was shown that the pyrolysis of dibenzyl itself, or side reactions with benzyl radicals, led to the formation of diphenyls under these conditions.

Any criticism that unfavourable reaction conditions were used, in which such secondary reactions could take place in the toluene pyrolysis, were refuted by the observation that at no time was the involatile fraction found to be free from diphenyls; even when 0.075% decomposition was obtained. Furthermore it was pointed out that the reaction

$$H + C_7H_8 \longrightarrow C_6H_6 + \cdot CH_3$$

has not been observed in any other system where a reliable source of hydrogen atoms was available, and if the (C-H) bond dissociation energy is significantly higher, it would seem more probable that the formation of methane could be ascribed to the process

$$C_6H_5CH_3 \longrightarrow C_6H_5 + \cdot CH_3 \quad \ldots\ldots\ldots (6)$$

proceeding simultaneously with reaction (1) postulated by Szwarc. The pyrolysis of dibenzyl in the presence of toluene resulted in the production of considerable quantities of hydrogen and no methane, an observation which tends to confirm this view.

The presence of stilbene in the reaction products from the pyrolysis of dibenzyl at temperatures at which toluene itself undergoes

decomposition suggested that dibenzyl existed in the furnace. If this were so then the Ea for the reaction,

$$Ph.CH_2.CH_2.Ph \longrightarrow Ph\,CH_2 - \quad + \quad Ph\,CH_2 -$$

would have to be considerably higher than that calculated based on the value of 77.5 Kcals/mole for the toluene bond dissociation energy. With all these complications present it was concluded that Ea = 90 Kcals/mole could not be ascribed to any single step involving the rupture of a bond.

b) The Bromination of Toluene.

Van Artsdalen[73] has studied the homogeneous gas phase kinetics of the thermal, and photochemical bromination of toluene. Analysis of the products obtained from this reaction showed that they consisted entirely of HBr and benzyl bromide, and, in addition it was demonstrated that no bromotoluenes were present, thus showing the reaction to be a side chain bromination.

Both investigations were undertaken at low temperatures, the photobromination being accomplished over the range 82 - 132.6°C, and the thermal bromination at 166°C. The reaction was found to be independent of total pressure, and proportional to the square root of the incident light intensity. In addition the presence of added HBr had a marked inhibiting effect.

In the photochemical reaction the rate of loss of bromine could be expressed by the equation;-

$$-d(Br_2)/dt = \frac{k\,(Br)^{\frac{1}{2}}(RH)^{\frac{1}{2}}}{1 + n(HBr)/(Br_2).} \qquad (a)$$

For the thermal reaction the data were computed from the equation;-

$$-d(Br_2)/dt = k(Br)^{\frac{1}{2}}(RH). \quad - - - \quad (b)$$

By considering the above observations, and working from analogies with similar studies on other hydrocarbons, the following mechanism was proposed:

	Br_2	+ hv	⟶	2Br		(1)	
or	Br_2	+ M	⟶	2Br	+ M	(1a)	
	Br	+ RH	⟶	R	+ HBr	(2)	2.2 Kcals/mole
	R	+ Br_2	⟶	RBr	+ Br	(3)	
	R	+ HBr	⟶	RH	+ Br	(4)	5 Kcals/mole
	Br	+ Br	+ M ⟶	Br_2	+ M	(5)	

(where M represents any molecule present.)

Analysis by the application of steady state conditions leads to the kinetic law; -

$$-d(Br_2)/dt = \frac{k_2 \dfrac{(RH)(aI/k_5(M))}{}}{1 + k_4(HBr)/k_3(Br_2)} \qquad (c)$$

where I is the intensity of the incident light and a the effective fraction absorbed.

By arranging the experimental conditions such that (tol) $\gg$ (Br) (therefore $k_5(M) = k_5(tol)$.) and maintaining constant light intensity, equation (c) is reduced to (a). Likewise, if the assumption is made that for extremely small percentage decompositions the HBr produced has a negligible inhibiting effect, then the corresponding thermal equation can also be derived.

The overall average Ea for the reaction was found to be 7.2 K cals/mole leading to a value of 2.2 K cals/mole for reaction (2), and this value, taken in conjunction with the dissociation energy of HBr yielded 89.7 K cals/mole for the (C-H) bond dissociation energy in toluene.

This work was published before that of Steacie's and the suggested value, D(C-H) = 90 K cals/mole obtained by him would seem to support it.

Ferguson[74] studied the pyrolysis of toluene in a flow system using nitrogen as the carrier gas. Like Szwarc and Steacie he based his calculations on the total quantities of gas formed. The gases, which were analysed by means of a mass spectrometer, were shown to contain 70% H_2 and 30% CH_4, in agreement with the proportions found by Steacie. However, the activation energy derived from the Arrhenius plot agreed with Szwarc's value of 77.5 K cals/mole. No investigation of the nature and composition of the solid or liquid products was attempted.

INDIRECT METHODS.

a) PYROLYSIS OF DIBENZYL.

The heat of formation of the benzyl radical can be calculated as indicated provided the value of the (C-H) bond dissociation energy for toluene is known, :eg:

$$Qf(C_7H_8) + D(C\text{-}H) = Qf(C_7H_7) + Qf(H).$$

Conversely if the heat of formation of the benzyl radical is accurately known, then an accurate value for D(C-H) can be calculated. A possible convenient method of obtaining Bz radicals would be through the dissociation of dibenzyl.

Barbier[75] and Graebe,[76] in separate investigations distilled dibenzyl through a red hot tube, and reported the formation of toluene, stilbene, and a small quantity of phenanthrene. Both observed a 2:1 mol ratio of toluene to stilbene.

Horrex and Miles (77) re-examined this reaction using initially a static system. The extent of the dissociation was followed by measuring pressures on a quartz fibre manometer. The results showed that the process taking place was not a simple dissociation; secondary reactions were occurring, and further investigations were carried out in a conventional flow system. The further work showed the following products were produced:- gaseous- H_2 plus negligible quantities of methane: liquid- toluene, benzene and styrene, with possible traces of ethylbenzene: solid- stilbene and unchanged dibenzyl. Hydrogen was estimated by combustion in a CuO furnace; the proportion of styrene present was estimated, a) by absorption in degassed sulphuric acid, b) by bromination in glacial acetic acid, and finally c) by its U.V. absorption spectrum. The quantity of ethylbenzene was estimated by microfractionation of the mixture, and was not appreciable. These authors were handicapped by the fact that a U.V. spectrometer was not available for analysis until most of the work had been completed by less accurate methods. The solid product was shown to consist entirely of stilbene and unchanged dibenzyl, the stilbene being estimated by bromination.

It was concluded from the quantities present that the overall decomposition could be represented by the equation:-

$$3\ C_6H_5CH_2CH_2C_6H_5 = 2\ C_6H_5CH_3 + C_6H_6 + C_6H_5CH{=}CH_2 + C_6H_5CH{=}CHC_6H_5$$

The reaction rate was independent of contact time, surface to volume ratio, and partial pressure of dibenzyl. The Arrhenius plot, log k v $1/T^{\circ}A$ yielded an activation energy of 48 K cal/mole, and a frequency factor $A = 10^{9.3}$.

This activation energy was ascribed to the rupture of the central C-C bond, and as was pointed out, this yields the same value for the resonance energy as was previously calculated by Szwarc.

Using the above value for the heat of dissociation of dibenzyl in conjunction with Qf = 28 K cal/mole for the heat of formation of dibenzyl we may compute $Qf(C_7H_7)$ as follows:-

$$Qf(C_6H_5CH_2) = D(Bz\text{-}Bz)/2 + Qf(DB)/2$$
$$= 38 \text{ K cals/mole.}$$

This value together with Qf(H)= 52 K cals/mole and Qf(tol) = 11.95 K cals/mole allows us to obtain the toluene bond dissociation energy

$$D(C\text{-}H) = Qf(Bz) + Qf(H) - Qf(tol)$$
$$= 78.05 \text{ K cals/mole}$$

in complete agreement with Szwarc's value obtained by pyrolysis. As pointed out by these authors the experimental frequency factor is abnormally low. Frequency factors for normal homogeneous first order decompositions usually agree to within a factor of ten with the value predicted by theory :ie: 10^{13}. A recalculation of Ea assuming $k = 10^{13} e^{-E/RT}$, and using the experimental value of k at 750°C, yields Ea = 65 K cal/mole. This in turn makes the (C-H) bond dissociation energy for toluene = 86 K cal/mole, more in line with the value proposed by Van Artsdalen.

This reaction has been more fully investigated by R.N.Pittilo[57] using more refined methods of analysis. His results suggested that the ratio of products varies with the partial pressure of dibenzyl, secondly, the true reaction order is 1.5 rather than first. Further work by Davidson[91] has indicated that $D(PhCH_2\text{-}CH_2Ph)$ may be of the order of 57 K cals/mole.

TABLE (8).

Compound	a	b	$D^{c}(PhCH_2-X)$	$D^{d}(PhCH_2-X)$	$D^{e}(PhCH_2-X)$	$D^{f}(PhCH_2-X)$
Toluene	11.8 ev	8.51 ev	77.0	77.5	95	89
Ethylbenzene	11.2 ev	8.51 ev	62.3	62.3	80	-
Dibenzyl	10.5 ev	8.51 ev	48.0	48.0	63.9	68

Key

(a) Appearance potentials of $PhCH_2^+$ from $PhCH_2$ - X.

(b) Ionisation potentials of $PhCH_2$- deduced (but not measured directly) from (a).

(c) Bond Dissociation Energies deduced from data (a).

(d) " " " from pyrolysis data of Szwarc.

(e) " " " deduced from (a) using a measured value of I ($PhCH_2^+$) = 7.73 ev. due to Lossing.

(f) Bond Dissociation Energies deduced using Van Artsdalen's value of D ($PhCH_2$ - H) = 89 K cals/mole.

DETERMINATION OF THE TOLUENE BOND DISSOCIATION ENERGY FROM IONISATION POTENTIALS.

Several studies have been made with a view to finding out the ionisation potential of the benzyl radical. As mentioned previously, the appearance and ionisation potentials are related by the expression:-

$$A(Bz^+) = D(Bz-X) + I(Bz+) + E - - - (Bz = PhCH_2-)$$

where E represents any kinetic energy with which the ionised particles may be formed.

Stevenson[77] determined the appearance potential for the production of the $C_7H_7^+$ ion from toluene, ethylbenzene, and dibenzyl. The values obtained are listed in column 2, table 8. The availability of the toluene and dibenzyl appearance potentials allows the ionisation potential for the benzyl radical to be calculated without reference to either the toluene or dibenzyl bond dissociation energy as shown below:-

$$tol \rightarrow Bz^+ + H + e, \quad A_1(Bz^+) = D(Bz-H) + I(Bz^+),$$

$$DB \rightarrow Bz^+ + Bz + e, \quad A_2(Bz^+) = D(Bz-Bz) + I(Bz^+),$$

Subtracting

$$DB + H \rightarrow tol + Bz, \quad Q = A_2(Bz+) - A1(Bz^+).$$

Taking the same values for the heat of formation of toluene and dibenzyl used before and D(H-H) = 4.48 ev, it follows that:-

$$DB + 2H \rightarrow 2\ tol. \quad Q_1 = -4.66\ ev.$$

and therefore

$$D(Bz-H) = 77.0\ K\ cals/mole \qquad I(Bz^+) = 8.51\ ev.$$

Lossing[8] however has pyrolysed (BzI) benzyl iodide in a retractable furnace mounted in the mass spectrometer head, and finds I(Bz+) = 7.73 ev instead of

8.51 computed above, and claims to have confirmed this value by work on other compounds. Using this latter value in conjunction with the appearance potentials listed by Stevenson, a different set of bond dissociation energies are obtained. (Col. 6). These results disagree when compared with other (Col. 7) possible values for D(Bz_2-H), and D(Bz-Bz), (latter based on D(Bz-H)=89 K cals/mole.) Unfortunately, Lossing has not yet published his value for the appearance potential of the Bz_2^+ ion derived from BzI. This when available, together with D(Bz-I)= 29.5 K cals/mole should provide a valuable cross check on the ionisation potential. The calculated value $I(Bz^+)^{(82)}$ = 7.98 ev is more in agreement with Lossing's value.

THE MASS SPECTROMETER.

As will be shown later, the mass spectrometer was used in this investigation as an analytical tool for the estimation of solids, liquids, and gases. Since this instrument is also used in the determination of bond dissociation energies by electron impact, it might be appropriate at this point to consider the general principles governing its operation.

General theory.

Consider an ion of mass m, and charge e, initially at rest and subjected to an accelerating potential gradient X. On passing through the potential gradient the ion will attain a kinetic energy:-

$$K.E. = \tfrac{1}{2}mv^2 = Xe. \qquad \ldots\ldots\ldots (1)$$

(where v is the velocity of the ion.)

If the ion then enters a uniform magnetic field of strength H, (gauss) the lines of force of which are perpendicular to the direction of motion, the ion will be subjected to a centrifugal force:-

$$mv^2/r = Hev \qquad \ldots\ldots\ldots\ldots (2)$$

By eliminating the velocity we find that the resultant path will be defined by the equation :-

$$m/e = r^2H^2 / 2X \qquad \ldots\ldots\ldots\ldots (3)$$

where m/e is defined as the mass to charge ratio of the ion. It is readily seen that ions of different mass and charge can have the same mass ratio. For example carbon dioxide and propane, CO_2 & C_3H_8.

In general however for ions of different mass ratio we will get a series of homogeneous beams of ions each of radius defined by the quantities on the R.H.S. of equation 3.

Under normal operating conditions the radius of the beam is defined by the geometry of the instrument, and either the magnetic field H, or the electrostatic field X varied. For a constant accelerating potential equation 3 therefore approximates to:-

$$m/e \propto KH^2.$$

and each mass ratio is defined by a particular value of the magnetic field. The variation of the magnetic field will focus each ribbon of ions in turn on to the collector slit system. In the most commonly used system the collector plate is earthed through an extremely high impedance. The potential created by the flow of electrons to neutralise the positive charge on the plate is then amplified by means of a D.C. amplifier, and recorded on the chart of an electronically operated pen recorder of the Honeywell - Brown pattern.

The deflection of this pen is proportional to the ion current, and hence to the quantity of each species present. By varying the magnetic field strength H, a series of peaks is obtained on the recorder chart. Under standardised conditions the relative magnitudes of these peaks are constant for any given pure compound, and are referred to as the mass spectrum or cracking pattern of that compound.

The cracking patterns of a great many hydrocarbon compounds have been published under the auspices of the American Petroleum Institute (Research Project No. 44.). For accurate analysis however it is still necessary to calibrate the apparatus with a known quantity of the pure material. The cracking pattern obtained depends on the electron bombarding voltage, the temperature of the ion source and the particular instrument. Furthermore the sensitivity of the instrument, defined in volts / mm backing pressure at the leak, varies from day to day, and must be experimentally found before commencing each set of analysis.

The accurate analysis of mixtures is even more difficult, and the following requirements must be met. If appreciable molecular discrimination occurs during the viscous flow through the leak into the instrument, then the relationship should be known between the partial pressures of the components in the sample, and their partial pressures in the ionisation chamber. The composition of the sample in the reservoir should not change during analysis, and the individual components which jointly contribute to a peak height should not mutually interfere.

In general, for accurate analysis of mixtures, it is usually best to make up a series of synthetic mixtures of the approximate composition of the sample, and compare the mass spectrum of the sample with those obtained from the synthetic mixtures.

A considerable number of excellent reviews[83] on the conditions required for the successful application of mass spectrometers to chemical problems have recently been published.

APPARATUS AND EXPERIMENTAL TECHNIQUE.

All the experiments were carried out in a continuous flow system using nitrogen as the carrier gas. The nitrogen pressure covered the range 2 - 10 mm mercury. The following is a general account of the apparatus and technique. Any specific modifications are described in the appropriate sections concerned.

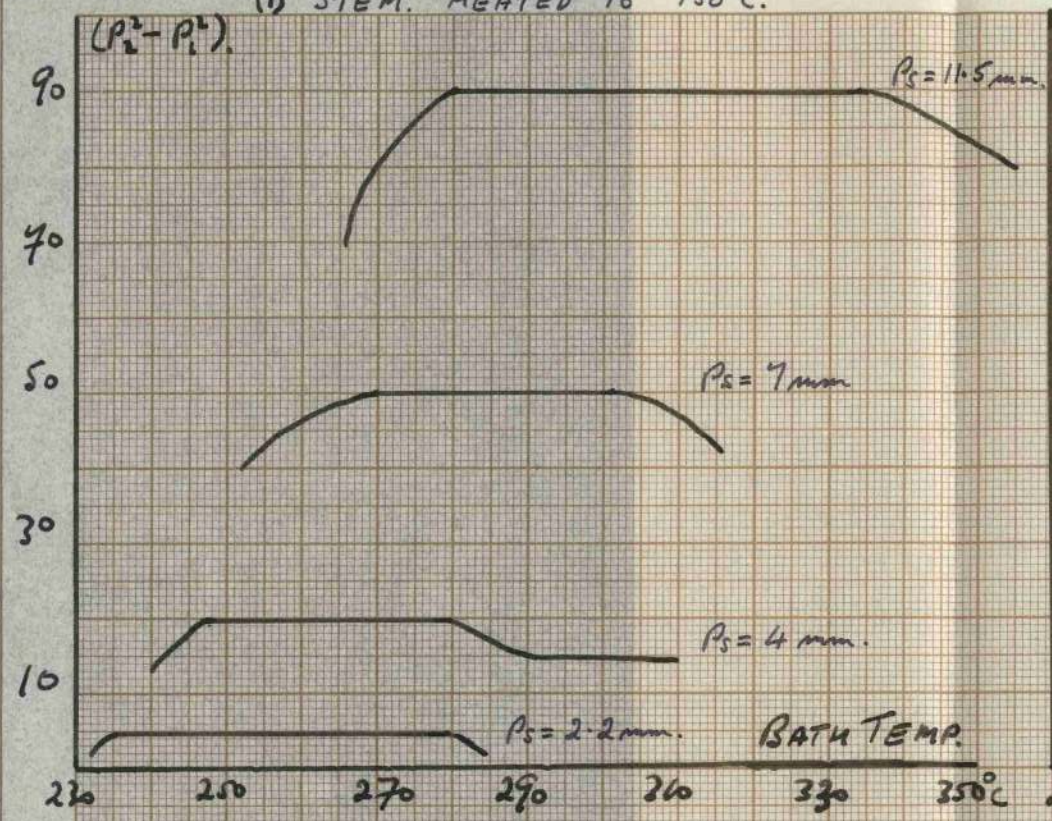
The Vacuum Line.

The apparatus was evacuated by means of a single stage mercury diffusion pump backed by a two stage Metropolitan-Vickers type D.R.1. rotary oil pump. A pressure of 10^{-7} cm of mercury could readily be attained and was measured by means of a McLeod gauge.

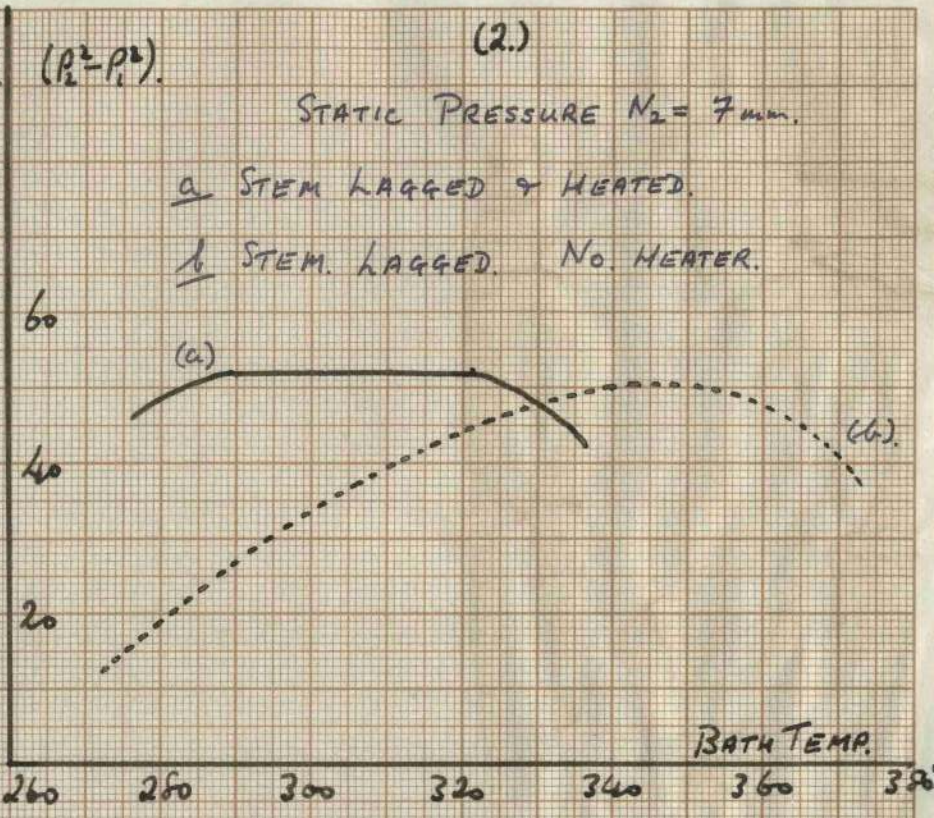
The Circulation Pump.

The carrier gas was circulated by a triple jet mercury diffusion pump. The boiler of the pump was maintained at $\pm$ 1°C by means of a solder bath, the power input to the bath being controlled by a Sunvic energy regulator type TYB. 1. Moore[84] has shown that the optimum performance of this type of pump depends on both the static pressure of carrier gas in the

(1) STEM. HEATED TO 130°C.



(2.)

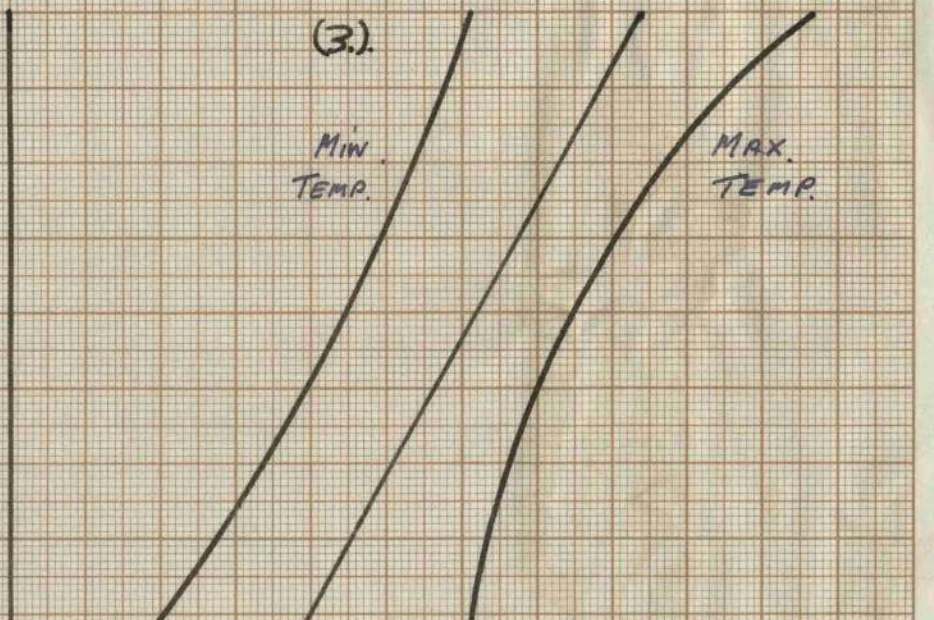


1) Variation in pumping rate with bath temperature.

2) Comparison of pump performance with & without heater on stem.

3) Optimum performance of pump; Static Pressure N_2 v Bath Temperature.

(3.)



system, and the bath temperature; the performance rising to a maximum and then falling off again. A plot of the rate of flow against bath temperatures at various static pressures of nitrogen is shown in fig. 1. It is easily seen from these curves that there is a small range of bath temperatures over which the performance of the pump is reasonably constant. Although the Sunvic energy regulator is capable of holding the bath temperature to the above limits, the ultimate temperature of the bath for any setting of the regulator depends also on the rate of heat loss to the surroundings, and thus on the room temperature. Unfortunately the daily variation of the ultimate bath temperature was outwith the range over which the pump performance was constant, and a few experiments were undertaken to see whether the critical temperature range could be increased.

Initial trials with the pump had shown that the addition of a second layer of asbestos lagging to the exposed stem slightly improved its performance. This stem normally attained a temperature of 130°C and accordingly an electric heater was wound on top of the asbestos, and another layer of asbestos placed over this for further insulation. By means of this heater the pump stem could be uniformly maintained at a temperature of 130°C when the pump was off, the principle being similar to the thermal jacket of the Fenske column. A comparison of the performance of the pump with and without the stem heater on is shown in Fig. 1.

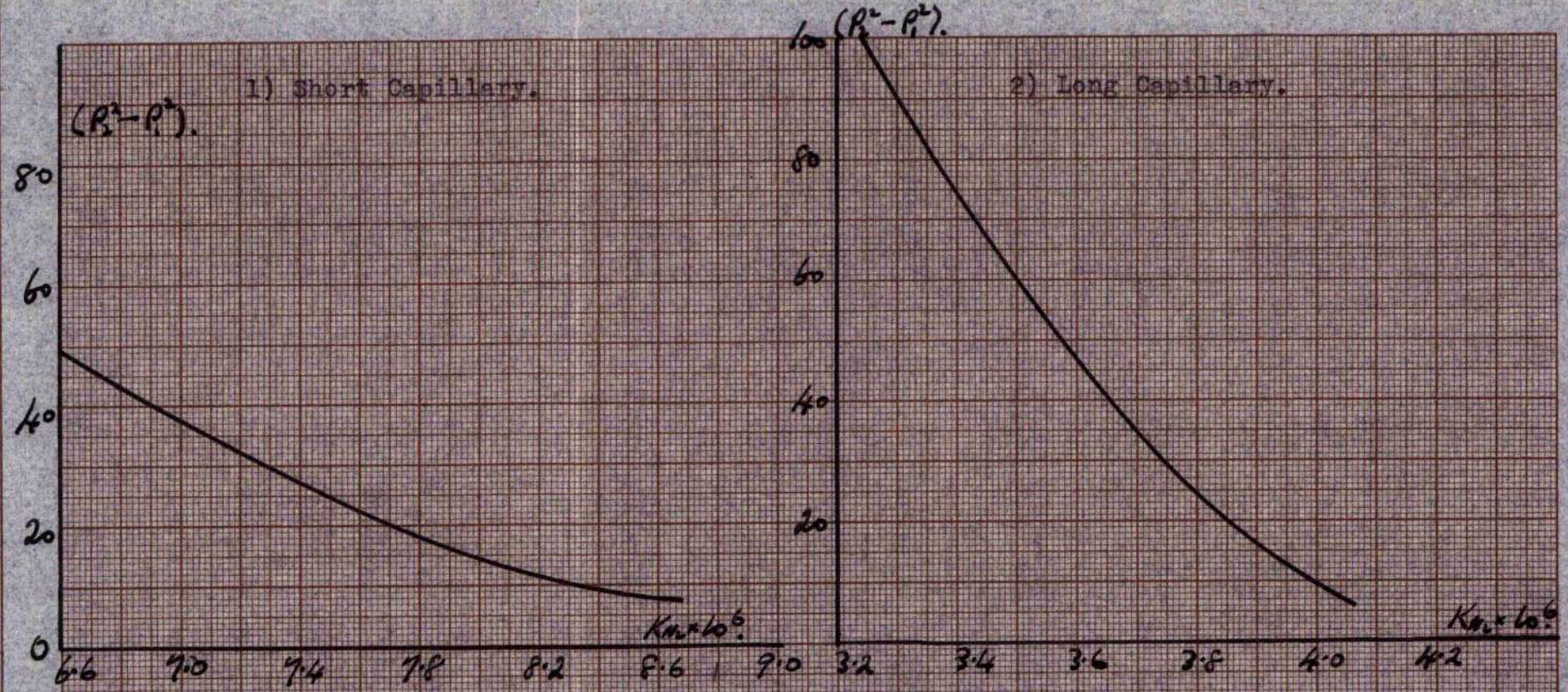
It is at once seen that the maximum speed of pumping has not altered, although the range of temperature over which it is constant has vastly increased from 5 to 40°C. Furthermore the mean temperature of operation of the bath has dropped from 315 to about 285°C thus lessening the tendency of the solder to oxidise, and prolonging the life of the bath. Likewise, the overall power consumption has dropped.

A possible explanation of the phenomenon is as follows. As the number of Mercury atoms leaving the jets increases, the number of collisions and hence total transfer of energy will increase, and this in turn maintains an increased rate of flow. Ultimately however under equilibrium conditions the carrier gas molecules passing through the condenser and past the jets will suffer the maximum number of collisions possible, and provided the rate of flow of mercury is not too high, will pass down the condenser without losing this kinetic energy by impact with a colloidal mist of cooled mercury. However as the temperature of the bath is further increased the rate of flow of mercury atoms through the jets increases to such an extent that the condenser space is congested with a colloidal mist of mercury vapour. The carrier gas molecules will therefore find it increasingly difficult to penetrate this without losing a large amount of their newly acquired kinetic energy and the rate of flow of carrier gas will decrease.

When the pump is run with its stem electrically heated, virtually all of the atoms evaporating from the mercury surface reach the jets after attaining thermal equilibrium with the stem. This

results in a much steeper rise in the rate of pumping, but at a certain critical value, dependent on the large resistance to flow in the external capillaries, the rate of flow reaches a maximum and constant value. The pump itself is capable of a much higher speed of pumping over this range and with a wider capillary would give a higher rate of flow for the same static pressure, and the same bath temperature. At the high temperature end, the greatly increased concentration of mercury vapour in the vicinity of the jets offers a resistance to the passage of the carrier gas and greatly slows down the pumping speed. When the performance of the pump falls below the critical value set by the system the flow curve will fall off as shown. The bath temperature at which this fall in performance occurs will therefore be lower in the case where the stem heater is on, since a far greater number of mercury molecules will reach the jets.

Rate of Flow and Gas Measurement. With the circulating pump operating at its maximum efficiency the rate of flow of carrier gas through the system was controlled by capillaries K_1 and K_2. The insertion of either, or both simultaneously, by opening taps 10 and 11, conveniently provided three rates of flow. Meyer has shown by a modification of Poiseuilles Law that it is theoretically possible to calculate the rate of flow through a given capillary, and relate this to the gas pressure at the ends, provided the physical constants of the capillary are known.



Capillary Constants.

Cap.	Radius Cm.	Length Cm.	K_{N_2} Calc.
Short	·1557	6·15	7·803.
Long	·1557	13·47	3·503.

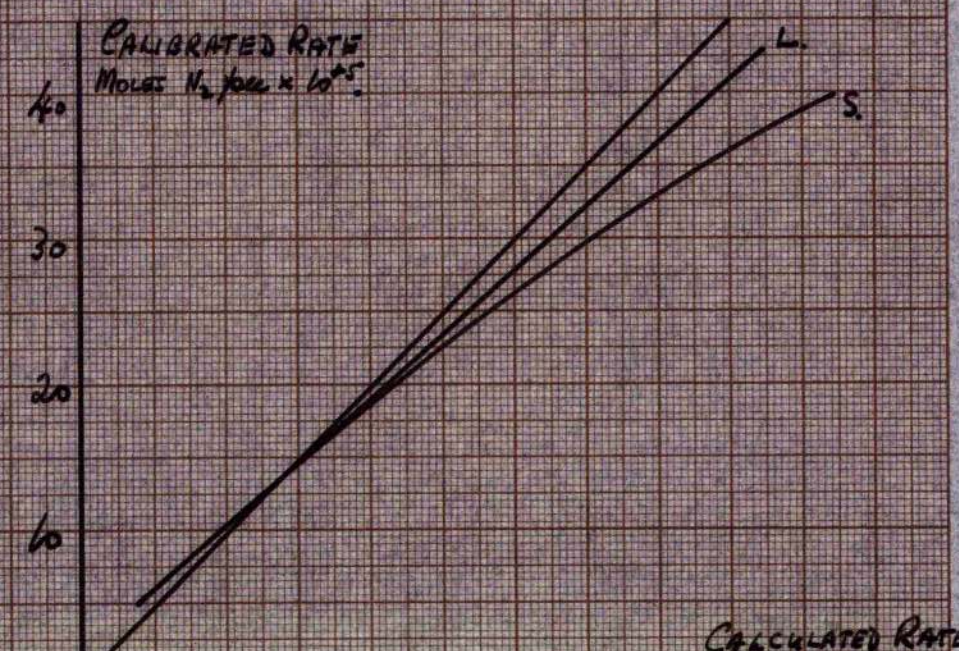


Fig 2.

The number of ~~gas~~ grain molecules flowing per sec

$$n = (\pi r^4(P_b^2 - P_a^2)) \quad / \ (16\ LRTm)$$

where r= radius of the capillary in cm.

P_a & P_b are the pressures across the ends of the capillary in dynes/ cm.

m = the viscosity of the gas in poise.

L = the length of the capillary in cm.

R = gas constant

T = the absolute temperature

For a given capillary and a given gas this equation may be reduced to

$$n = k\ (P_a^2 - P_b^2\ ).$$

where the capillary constant $k = \pi r^4/16\ mRTL$.

Lapage[8] has shown that at low pressures there are marked deviations from the theoretical behaviour, and that in fact k is not constant. The capillaries were therefore calibrated in situ by passing a known volume of dry nitrogen through at a constant rate. The experimental k values thus obtained are shown in fig. 2.plotted against the rate of flow. In both cases the experimental values are lower than the theoretical at low circulating rates, and are higher at higher rates of flow. Cowan[8] has shown that such variations in the capillary constant are a property of the particular capillary chosen. In this case both capillaries were selected from the same piece of pyrex glass tubing and only their lengths differed. All the capillaries investigated by Cowan showed k values greater than theoretical for all

flow rates, Lapage, on the other hand, obtained a smaller rate of flow than that expected from theory. The phenomenon may be due to the surface nature of the glass and end effects of the mountings. Further experiments showed that the k experimental (= k.exp.) values for any other gas could be obtained by substituting the appropriate value for the viscosity in the experimental k obtained for nitrogen ;ie:

$$k \text{ exp, air} = k \text{ exp, } N_2 \cdot {}^{mN_2}/_{m \text{ air}}.$$

It was also verified for two capillaries in parallel that the combined k value = $k_b = k_1 + k_2$.

The pressures on either side of the capillaries were measured by means of McLeod gauges.

Purification of Nitrogen Carrier Gas.

Nitrogen from a cylinder was purified by passing it through a liquid air trap to remove condensible impurities, through two sodium traps heated to 300°C to remove oxygen, and then through a glass wool filter to remove any traces of sodium oxide, and stored in a five liter flask. Before use, to ensure freedom from oxygen, each batch of nitrogen was analysed by means of a mass spectrometer.

Determination of the average pressure of nitrogen in the furnace.

The calculations given in the appendix show that in order to evaluate the contact time, the average pressure inside the furnace must be known. Since this pressure cannot be measured directly by means of

a McLeod gauge, it was obtained by an experimentally derived equation relating it to pressures measured at other points in the system.

Pressures were taken at points A.B.C. and D. indicated in fig. 7. From the results obtained it was found that the average pressure could be estimated from the equation $P(av) = C + K(A-C)$ where $K = 0.1$. This equation assumes that the resistance to flow of the system between A. and C. remains constant, a condition only attained if the balls of both the injector units have been withdrawn from their seats by at least four complete revolutions of the threaded ring. For any setting less than this, a marked effect was noticed both on the rate of flow, and in the value of K in the above equation. In practice the balls were withdrawn from their seats by four and a half complete revolutions of the stem thread.

The equation was found to hold for either capillary and for all rates of flow.

The Reaction Vessel.

The reaction vessel was constructed of silica and had a coaxial thermocouple pocket. The internal diameter of the outer jacket was 26 cms, the length of the heated portion 59 cms, volume 298 ccs, surface area including the outer surface of the thermocouple pocket 565 sq. cms. It was joined to the rest of the apparatus by silica cones jointed to pyrex sockets by means of Edwards W.6 wax.

The Furnace Jacket.

This consisted of an inconel tube, 5 cms in diameter and 61 cms long, insulated with two layers of asbestos paper and a quarter inch layer of alundum cement. The heating element of nichrome tape was wound on this base in five

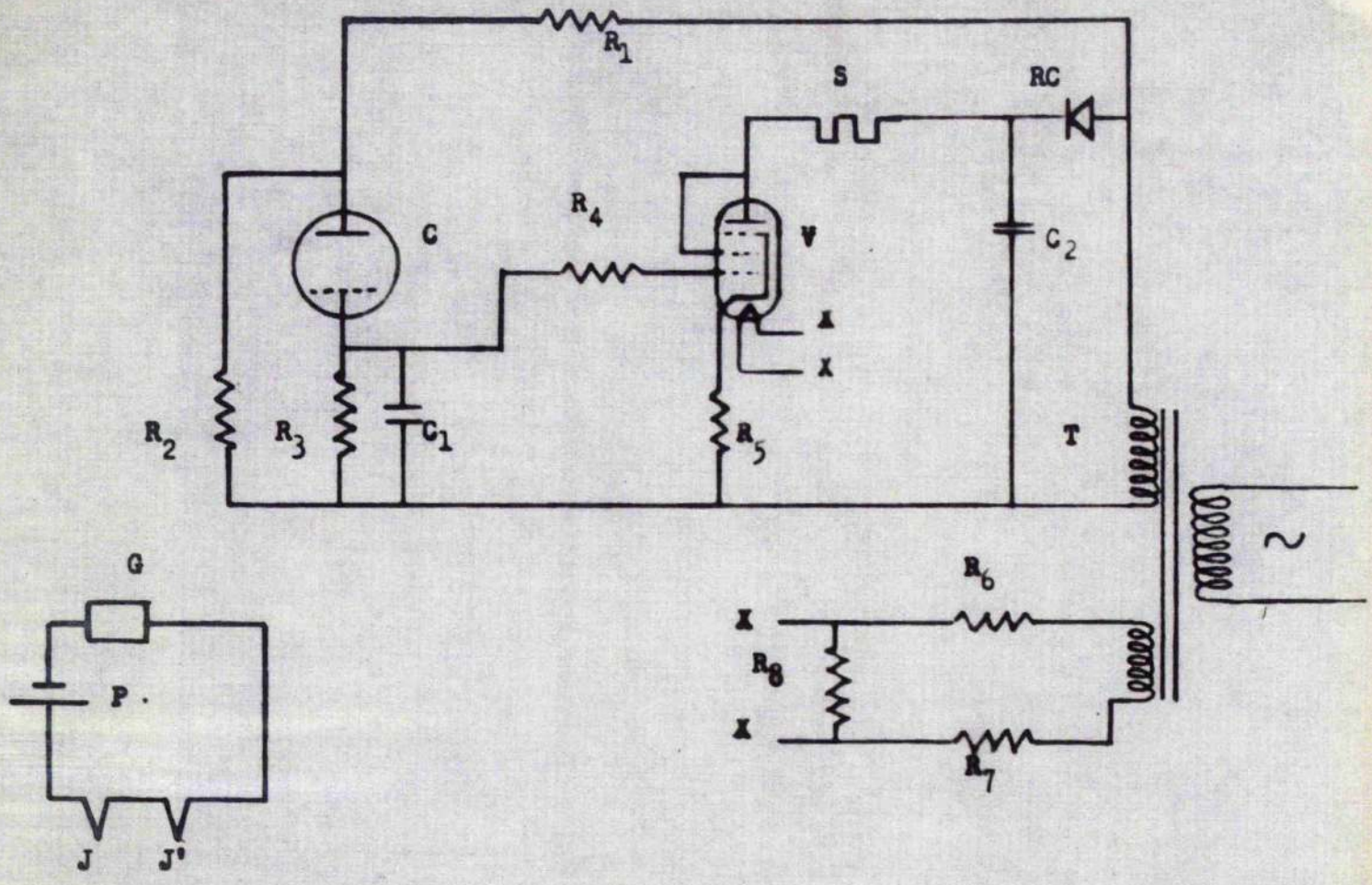
sections. In the three inner sections the turns were uniformly spaced 1 cm apart, and the two end sections were wound exponentially to compensate for the greater heat losses at the ends of the jacket. A second layer of alundum cement quarter of an inch thick was applied, and the whole further lagged with a two inch thick asbestos steam pipe casing.

By placing appropriate shunts across each section a constant temperature of $\pm 1^{\circ}$ C could be obtained along the length of the furnace.

Temperature Control.

Temperature control of the furnace during runs was achieved by the use of the electronic furnace controller described below. Due to the amount of lagging round the furnace jacket, and in particular between the nichrome tape and the reaction vessel, the thermal delay in the heating or cooling of the jacket markedly reduced the sensitivity of the controller. For this reason the controlling element had to be brought nearer the temperature sensitive element (in this case the thermocouple) and accordingly an auxiliary heater of nichrome tape was wound directly on to the silica reaction vessel. Using this auxiliary heater, and passing a current equivalent to twenty per cent of the total power dissipated by the outer furnace jacket, the temperature of the reaction vessel could be maintained constant to $\pm \frac{1}{8}^{\circ}$ C (provided the reference D.C. source, in this case a Pye potentiometer, remained reasonably constant.)

(The choice of 20% of total current was taken because of possible voltage reductions of up to 20%). The temperature of the furnace was measured by a chromel - alumel thermocouple, which was also used as the temperature sensitive element for the electronic controller. The E.M.F. of this chromel-alumel thermocouple was measured at the standard temperatures listed below (Table 9), and the results checked against those of Roeser, Dahl, and Gowens.[92]



Components.

P.	Pye Potentiometer.	R_1.	25 K ohms.
G.	Pot Galvo 20 ohms.	R_2.	4.7 K "
C.	Cintel Photocell G.S.16.	R_3.	5 MEG "
T.	Pri 240v sec 240 v. 50 M.A. 20v. 2A.	R_4.	47.0 K "
V.	N.78.	R_5.	1 K Pot.
R.C.	Rectifier 250v 0.1A.	R_6.	12 volt 24 watt lamp.
S.	Sunvic Switch 602.	R_7.	1 ohm.
C_1.	0.05 mfd.	R_8.	4.62 ohms.
C_2.	6.0 mfd 300v WG.		

fig. 4.

As the deviations were found to be negligible the values quoted by them for the range 0°C - 1400°C were used.

TABLE 9.

Metal	Melting point °C	Measured E.M.F. millivolts
Tin	231.9	9.41
Lead	327.4	13.35
Zinc	419.4	17.22
Antimony	630.5	26.18

Electronic Temperature Controller.

The circuit shown in fig.4 is a modified version of a temperature controller circuit designed by Shepherdson.[87] The original photocell, G.E.C. type CWS.24, was found to be obsolete and was replaced by a Cintel 16.

The general principle of the controller is as follows. The output E.M.F. of the potentiometer is set at the value generated by the chromel alumel thermocouple at the required temperature. When the reaction vessel has attained this temperature the E.M.F. of the thermocouple is balanced against that of the potentiometer so that there is no deflection of the mirror galvanometer. Under these conditions the vertical image of the filament of the galvanometer bulb is focussed on to the vertical slit of the photocell; the photocell conducts and raises the negative voltage applied to the grid of the valve. This in turn drops the anode current of the valve below the critical value required to operate the Sunvic vacuum switch and this, on opening, cuts off the auxiliary heater.

As the reaction vessel cools and falls below the desired temperature, the image is deflected off the photocell slit, the valve again conducts, the hot wire vacuum switch closes, and the auxiliary element is switched on. The galvanometer is arranged so that, when the image falls on the photocell slit, the galvanometer coil engages in its stop. The image is therefore prevented from overshooting the slit, and so further heating the already too hot reaction vessel.

The electrical circuit is arranged so that failure of the galvanometer lamp immediately cuts off the current to the auxiliary heater, and prevents overheating of the reaction vessel. Apart from the provision of an extra 5 megohm resistance in the anode circuit, to allow for photocell deterioration, no further precautions were taken.

A 10% reduction in the mains supply voltage was sufficient to drop the anode current of the valve below the critical value required to operate the Sunvic vacuum switch. It was therefore found necessary to include a half wave metal rectifier and a condenser in the H.T. circuit rather than use the valve as its own rectifier. Possibly a cheaper alternative would have been to place a resistance in parallel with the valve. However, the increased plate current rendered the operation of the controller independent of the most severe voltage reductions.

Ball Valve Injector Units.

Since toluene vapour readily dissolves in tap grease, and iodine is first absorbed and then reacts with most vacuum greases, it was necessary to devise an injector system which had the following properties;

(a) it should be capable of being heated to 150^{o}C in order to furnish sufficient vapour pressure for an injector capillary without the injected material

condensing out inside it;

(b) it should be constructed of materials which neither absorb nor react with toluene or iodine;

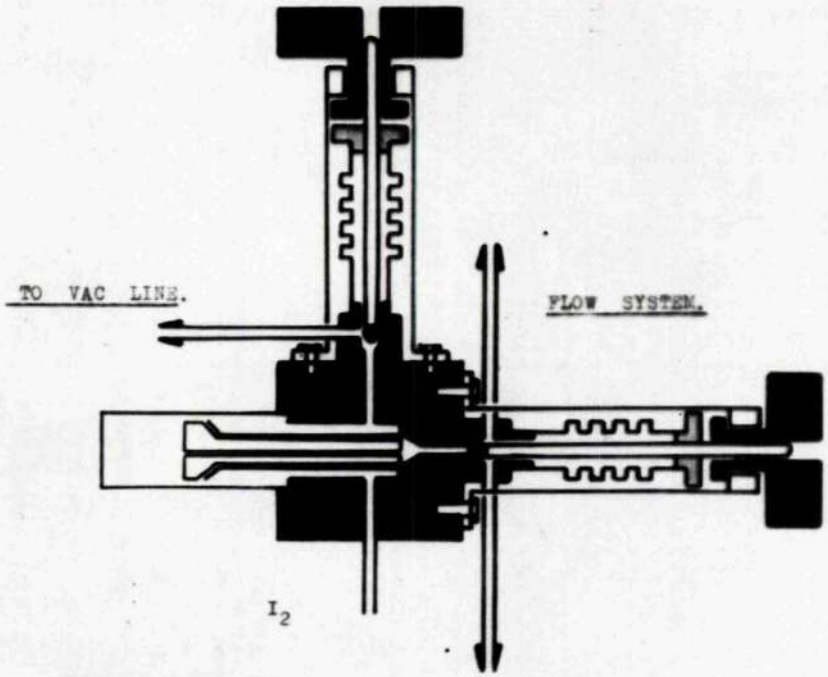
(c) it should be possible to isolate and free the reactants from dissolved gases under high vacuum conditions.

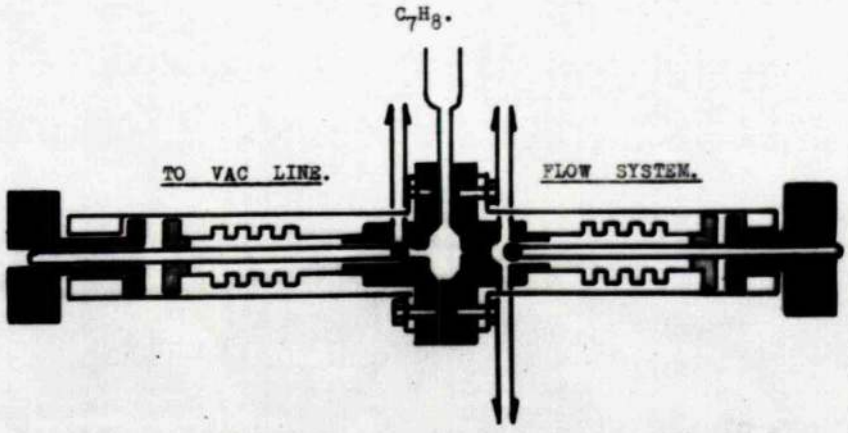
Three possible systems were considered:-

(1) All glass thermostatically controlled saturators through which the carrier gas flows picking up the vapour of the substance. Normally with two substances a split flow technique is used. In this method the carrier gas stream is split, flows through the saturators arranged in parallel, and then meets again before passing through the furnace. In order to obtain consistent results, the saturators have to expose a large surface area to the carrier gas and therefore are of fairly large physical dimensions. (Sometimes two are used in series for each substance.) This introduces difficulties with toluene which would have to be immersed in liquid air in order to obtain the low pressures required for degassing before commencing a run. The idea was therefore rejected.

(2) A second possibility was the construction of an all glass system by means of which the reactants could be injected through a capillary into the gas stream. Such a system involves the use of greased taps and was therefore rejected, although a system of this nature was built and used for the injection of hydrogen iodide which is only slowly absorbed by tap grease.

(3) The third possibility is really a modification of the second; a system comprising of metal ball valves, entirely constructed of corrosion resistant metals, and joined to the reactant containers by metal to glass seals.





INJECTOR UNITS.

fig 5.

After several prototypes had been tested and found unsuitable, the injector shown in fig. 5 was found suitable for the injection of toluene vapour into the system. The body of the valve was constructed of mild steel, and the bellows of stainless steel. The valve could be opened, closed or evacuated by screwing down the appropriate stainless steel ball bearing tipped rods on to pre-shaped copper seats.

It was found more convenient to use a No. 17 stainless steel hypodermic needle as the jet rather than drill a small hole nine thousands of an inch in diameter in the copper seat. All joints were either brazed or soldered with a variety of silver alloys in such a manner that the bellows could be removed without impairing the vacuum tightness of any of the other joints. The entire valve could be heated to 150°C or more by means of the electric heaters on the seamless steel tubes protecting the bellows and on the main valve body itself. Before installation each valve was tested for leaks on a mass spectrometer.

With a needle of such small internal diameter as the jet, a backing pressure of 50 mm was required in the toluene reservoir to obtain a pressure of 0.1 mm in the carrier gas stream. (N_2 partial pressure approximately 4.8 mm). The rate of flow of gases through a capillary may be approximately expressed by the equation;

$$n = k\,(P_1^2 - P_2^2)$$ (See previous discussion Pages 44)

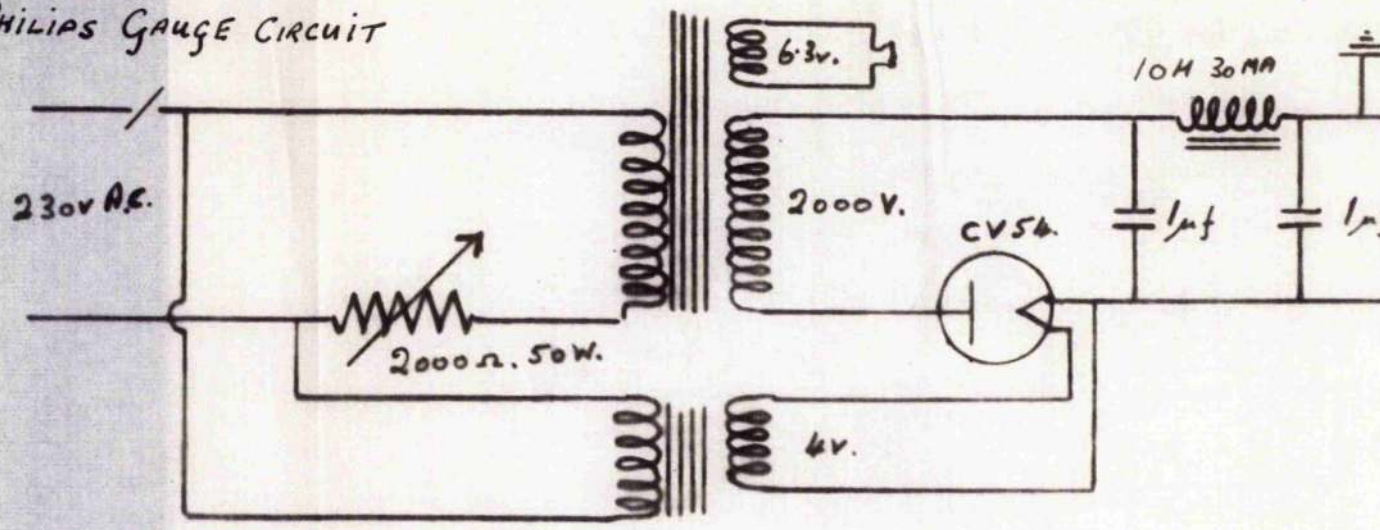
It is therefore seen that small variations in the pressure of the carrier gas passing the mouth of the capillary will have a negligible effect on the rate of flow of toluene through the capillary, provided the backing pressure is high, as it is in this case.

The appropriate exits of the injectors were joined to the rest of the

apparatus, or to the reservoirs, by means of metal cones and glass sockets jointed with Edwards No. 6 wax, or by Nilo K glass to metal seals.

Trials with the second valve using iodine in the reservoir showed that the stainless steel hypodermic needle slowly disintegrated in the presence of iodine vapour, although the rest of the valve remained unaffected. This difficulty was solved by modifying the body of the valve so that it could contain a glass capillary shaped and ground to fit into a mild steel holder, and held in position with silver chloride cement. This cement is completely unaffected by high concentrations of iodine vapour. The body of the valve was so constructed that the capillary could easily be removed and replaced by another of different internal diameter if required. This valve was heated in a manner similar to that for the toluene valve and again all the joints were soldered with the appropriate silver alloy. The toluene and iodine reservoirs were each heated by means of two constantly stirred small thermostats, ($5" \times 7"$) and were each controlled to $\pm \frac{1}{4}^{\circ}C$ by Sunvic bimetallic stem thermostats. Initially some trouble was experienced with these controllers. The iodine thermostat was oil filled and operated in the region 90- 110°C. It contained two heating elements, the main one wound on the outside and an auxiliary one immersed in the oil and controlled by the Sunvic thermostat. The ultimate temperature varied from day to day and creeping occurred during a run. This fault was finally shown to be caused by the conduction of heat along the stem to the head of the thermostat which contained the temperature setting device. In the initial experiments the thermostat stem was almost fully immersed in the oil and the head attained a temperature approaching 60°C by conduction. Since the temperature sensitive element only extends about three inches along from the tip of the stem, the

a) PHILIPS GAUGE CIRCUIT



b) PIRANI CIRCUIT.

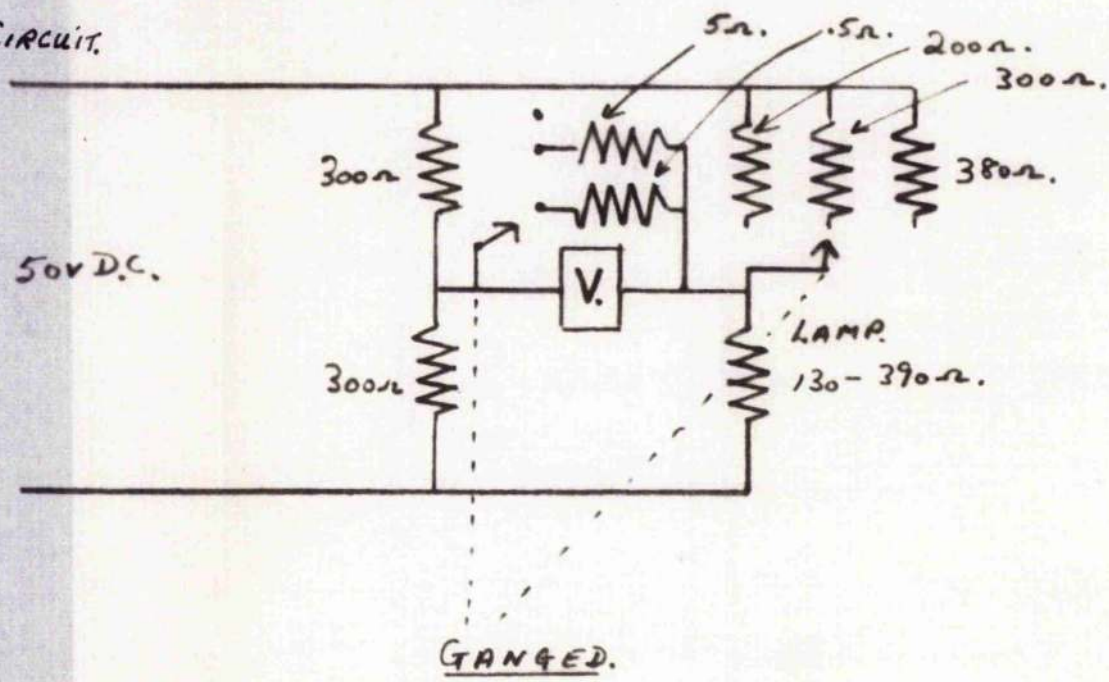


fig 6

stem was withdrawn several inches and a copper collar inserted between the base of the head and the retaining flange on the copper thermostat can. This dissipated most of the heat before it reached the head and allowed the head to run at room temperature. The modification eliminated the day to day variation in the setting, and also the drift experienced during operation.

The toluene thermostat operated in the region 20-40°C. Instability in the control of this thermostat was caused by electrical leakage down the stem of the stirring motor. Both Stirrers were isolated from their respective motors by "Tufnol" bushes. The results of trial runs done under constant conditions of nitrogen pressure showed that the output could be controlled to ±2 % and the concentration of the reactants in the furnace zone could be kept constant to an average of ± 2%.

During operation each valve with its associated inlet tubes was heated to approximately 50°C above the reservoir temperature to prevent condensation of the iodine or toluene in the interior of the valve or in the input lines.

Leak Detection.

Leaks in the glass parts of the apparatus were conveniently detected by using an Edwards H.F. Tesla coil. This instrument could not be used to test the metal valves, so in order to test them in situ, a Pirani gauge and a Philips gauge, were constructed.

The Pirani gauge consisted of an Ediswan squirrel cage 40 watt lamp attached to a B 14 cone, and jointed to the vacuum line by Edwards W.6 wax. The associated sensitive bridge circuit is shown in fig. 6. No attempt was made to stabilise the electrical supplies so that the meter readings could be

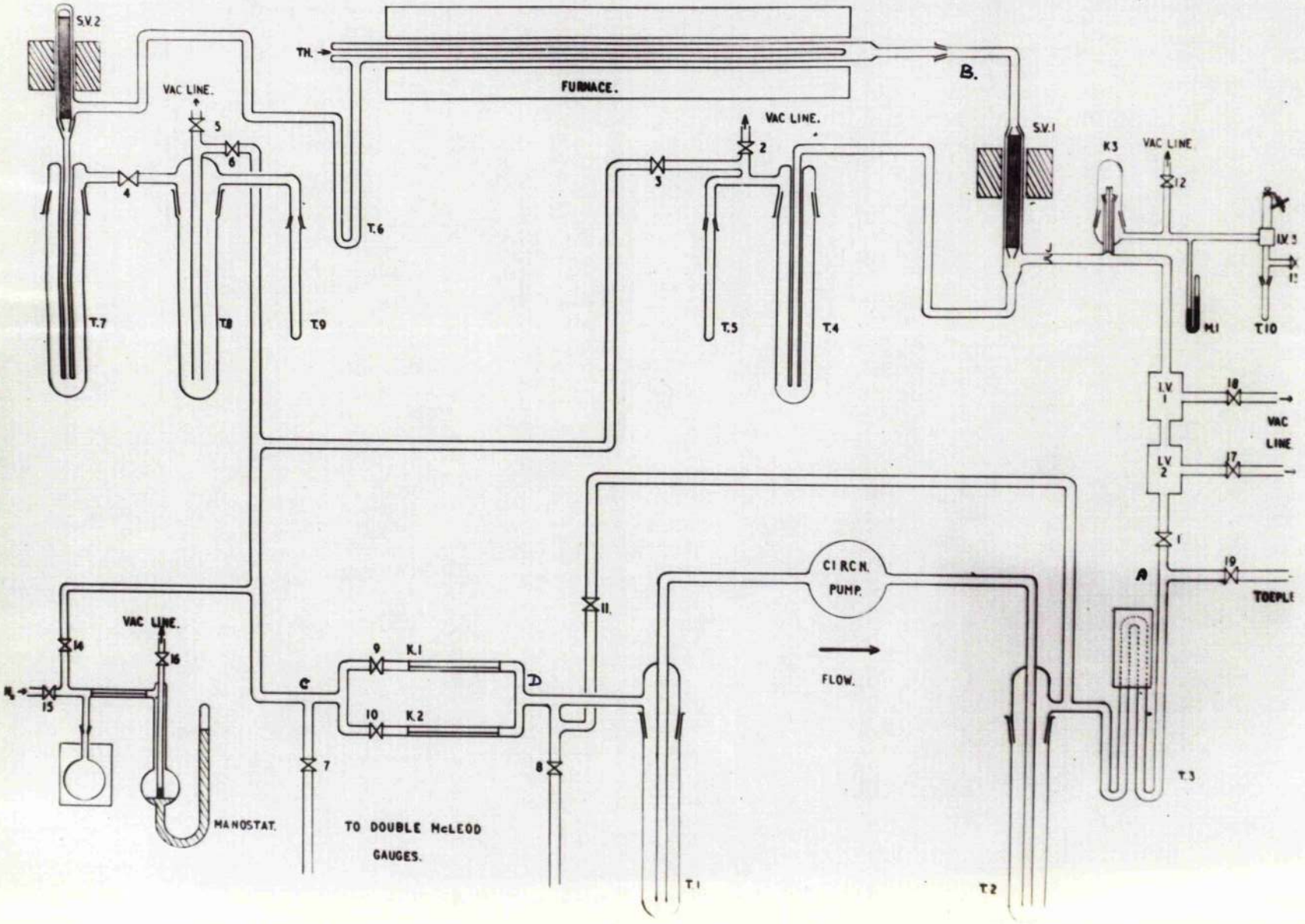

S.V.2
TH.
FURNACE.
B.
VAC LINE.
5
6
4
T.6
T.7
T.8
T.9
VAC LINE.
2
3
T.5
T.4
S.V.1
K.3
VAC LINE.
12
M.1
T.10
LV 3
11
LV 1
18
VAC LINE
LV 2
17
1
A
19
TOEPLE
CIRCN. PUMP.
FLOW.
11.
VAC LINE.
14
16
15
9
K.1
10
K.2
C
D
7
8
MANOSTAT.
TO DOUBLE McLEOD GAUGES.
T.1
T.2
T.3

fig 7

permanently calibrated against pressures. The gauge was merely used to show changes in pressure, and was not used for absolute pressure readings. Three pressure ranges were available (10^{-4} to 10^{-5}, 10^{-3} to 10^{-4}, 10^{-2} to 10^{-3} mm) by simultaneously altering the shunts across the meter, and the series resistances in the arm of the bridge.

For smaller leaks under much higher vacuum conditions a Philips gauge was used. A 2000 volt power pack was constructed for this gauge and the circuit is shown in fig.6. It consists of a half wave valve rectifier and a conventional inductance capacity smoothing stage. Pressure changes were indicated on the milliameter in the power pack, or (in the case of very low pressures) by means of an external microammeter.

Nitrogen Manostat.

It was found desirable to regulate the input of nitrogen to the system so that a constant quantity could be injected before each run. The system constructed is shown diagramatically in fig 7. By cautiously opening tap 15 nitrogen is slowly admitted from the nitrogen reservoir until the level of the mercury has fallen below the exposed surface of the sintered glass disk. Tap 15 is then closed and tap 16 opened to the vacuum line and the excess nitrogen in the manostat pumped out, the pumping automatically ceasing when the mercury covers the horizontal lower surface of the sintered disk. Tap 16 is then closed, and tap 14 opened to expand the nitrogen into the apparatus.

The sintered disk was made by grinding the projecting lip off the top of a 4 F micro filter stick. This material is sufficiently fine to prevent the passage of mercury, but is still porous enough to allow air to pass through.

To eliminate external temperature effects all connections between the

manostat and the other parts of the apparatus were made of fine diameter quill tubing. The bulb, which constituted the main volume was always immersed in ice.

By this means, a constant quantity of nitrogen could be admitted to the apparatus and the amount could readily be varied by changing the volume of the detachable bulb, or by repeating the operation and introducing a second dose of nitrogen.

Preparation and Purification of the Reactants.

In reactions in which toluene is used as a carrier gas and radical acceptor, Szwarc has shown that consistent results are only obtained if the toluene has been pre-pyrolysed by itself to remove impurities. The B.D.H. toluene used throughout these experiments was twice pyrolysed by passing it through a furnace maintained at 850°C (contact time 0.2 sec). The pyrolysed toluene was then dried over sodium, and subsequently distilled using a Fenske column. The fraction boiling in the range 110.7 - 110.9°C was collected.

The resublimed iodine used was manufactured by Whiffen. (B.P.C. quality). Apart from being subjected to prolonged pumping over acetone - CO_2 to remove traces of chlorine, no further purification was thought necessary.

Preparation of Hydrogen Iodide.

All the hydrogen iodide used in the investigations was prepared by slowly dropping a concentrated solution of iodine in 50% W/W hydriodic acid on to a mixture of dry red phosphorous and iodine. The hydrogen iodide evolved plus traces of iodine were distilled over and collected in a trap immersed in liquid air. On completion of the reaction, the trap was removed, attached to the apparatus in place of T_{10}, and thoroughly evacuated. The system was then isolated from the vacuum line, the liquid air removed, and the hydrogen iodide allowed to distil into a previously evacuated five litre flask which had been

coated with black paint on the outside to prevent the slow photochemical decomposition of the hydrogen iodide. The hydrogen iodide was stored in this reservoir until required.

Injection of Hydrogen Iodide.

The hydrogen iodide injection system is shown in fig. 7. T_{10} was immersed in liquid air and a sufficient quantity of hydrogen iodide distilled from the five litre flask through tap 13. Tap 13 was then closed and the liquid air replaced by CO_2 - acetone.

The hydrogen iodide was injected through K3, the rate of injection being controlled by the needle valve IV.3. The manometer M.1. allowed the fore pressure to K3, and hence the rate of flow to be accurately adjusted so that experiments could be repeated. In spite of this however, the rate of injection of hydrogen iodide was always estimated by means of a separate analysis run.

The hydrogen iodide injected in this manner was found to be completely free from traces of iodine. All the taps joining the hydrogen iodide injection system to the rest of the apparatus were lubricated with Edwards Silicone High Vacuum Grease, and in addition, 1 ml of Dow Corning 703 silicone pump fluid was placed on top of the mercury surface of manometer M.1 to protect it from any traces of iodine.

Collection of Products.

The products emerging from the furnace passed through a U tube, (T6) and then through the series of traps, T7 and T8 (see fig. 7) where the products were removed by selective freezing out. The traps T7,

T8, and T9, were arranged in triplicate, (the two other sets are not shown), so that three consecutive experiments could be performed without opening the apparatus to the air. The products could be passed through any one of the sets of traps by opening the appropriate independently operated all glass solenoid valve. These solenoid valves consisted of a plunger with a piece of soft iron sealed inside it. The plungers were raised or lowered by using a rheostat to alter the current through the solenoid.

The first trap in each series contained an internal heater of nichrome tape wound in the interspace in the double walled entrant tube. This heater prevented the products blocking the tube. In order to ensure that the most volatile products were completely stripped from the carrier gas, the second trap was loosely packed with glass wool.

In addition, a spare solenoid valve and trap were provided to collect unwanted products before each set of runs had commenced, and after they had finished.

Initial experiments showed that the exit gases from the furnace consisted of hydrogen iodide, stilbene, a little hydrogen, and unreacted toluene and iodine. The stilbene, being relatively involatile, condensed out in T6 round which was placed a dewar flask containing water at 10°C. At this temperature no iodine condensed out in T6 along with the stilbene.

The heater trap T7, which was immersed in acetone /CO_2, (-80°C) condensed out all the iodine and a little of the toluene, the remainder of the toluene and the hydrogen iodide condensing out in the liquid air trap T8.

The hydrogen, being incondensible in the liquid air trap, recirculated with the carrier gas, and was collected at the end of the run in a previously evacuated bulb, after being extracted from the flow system by means of a Toepler pump.

Analysis of Products.

a) The iodine deposited in traps T7 and T4 was dissolved in iodine free KI solution and titrated with frequently standardised N/10 sodium thiosulphate using freshly prepared starch as an indicator.

b) Several procedures were tried before a satisfactory method was obtained for the estimation of hydrogen iodide. Accurate estimation of the quantities of hydrogen iodide formed necessitated the use of N/100 reagent solutions.

A few trial experiments were performed using N/100 caustic soda and bromophenol blue, which appeared to be the most suitable indicator. Difficulty was experienced, however, in detecting the precise end point due to the indistinct nature of the colour change, and the method was rejected. The two other methods tried gave satisfactory results.

In the first N/100 silver nitrate was titrated against the hydrogen iodide in a cell containing two silver- silver iodide electrodes. The electrodes were coupled up to a titrimeter and the end point was indicated by full scale deflection on the microammeter. Further trials with potassium iodide in place of hydrogen iodide showed that the electrodes preserved their sensitivity indefinitely

provided they were immersed in distilled water when not in use. The titrimetric method was used to estimate the hydrogen iodide obtained in runs 1 - 140.

In the second method the hydrogen iodide obtained was immediately added to a solution of potassium iodate (iodine free) and the liberated iodine titrated with N/100 sodium thiosulphate using freshly prepared starch as an indicator. The iodine is liberated according to the following equation

$$6HI + KIO_3 = KI + 3I_2 + 3H_2O$$

and is removed as follows

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

This titration is carried out in an atmosphere of nitrogen as the absorption of carbon dioxide to form carbonic acid is followed by the liberation of more iodine due to the following reaction:-

$$6H^+ + 5NaI + KIO_3 = 3I_2 + 3H_2O + 5Na^+ + K^+.$$

The hydrogen iodide formed in runs 140 onwards was estimated by this method. The N/100 thiosulphate was freshly made up each day from the stock solution of N/10 thiosulphate used in the estimation of the iodine.

It is widely known that hydrogen iodide readily dissolves in toluene even forming complexes. Trial runs were undertaken by passing toluene together with excess hydrogen iodide through the apparatus under normal operating conditions but with the furnace cold. These conclusively proved that less than 0.1% was condensed out with the toluene in the -80°C trap T7.

c) On the completion of each set of runs, trap T6, which contained the stilbene and any other solid involatile organic solids, was cut off, and the deposit dissolved in specially purified methanol. This solution was carefully transferred to a graduated flask and made up to the mark. To remove traces of iodine, 0.05cc of mercury was added to the solution and the flask shaken vigorously. The flask was allowed to stand for five minutes and then further diluted.

The diluted solution was then examined in a Unicam U.V. spectrophotometer and the optical density at 308, 318, and 320mμ noted. These values, together with the appropriate extinction coefficients derived from the standard absorption curve for stilbene, (obtained by calibrating the instrument using pure stilbene), gave three values for the concentration of stilbene. The mean of these values was taken to represent the concentration of stilbene in the solution. A specimen of the calculations involved will be given later.

DESCRIPTION OF AN EXPERIMENT.

In order to eliminate zero drift and instability as much as possible, the high capacity accumulator (Exide type C.X.G.8) was charged each night and coupled up to the potentiometer twelve hours before it was required for a run. These precautions virtually eliminated any drift in the E.M.F. generated by the potentiometer to balance that from the thermocouple, and likewise ensured that the furnace temperature did not vary during the run. As an additional precaution the E.M.F. was frequently standardised while any experiment was in progress.

To allow the furnace to heat up, the furnace jacket heater was switched on six hours before the start of an experiment by means of a Venner time switch. The apparatus itself was pumped out for at least one hour during which time the iodine and toluene thermostat baths, and the circulating pump bath were allowed to heat up to the required temperatures. The furnace controller was also set to the required temperature. The methyl alcohol in traps T_9 (purified as suggested by Naylor[68]) was outgassed by freezing in liquid air, opening the appropriate taps, (tap5), and pumping out. The taps were then closed, and the alcohol allowed to warm up thus releasing the dissolved gases, whereupon the alcohol was refrozen, and the liberated gases pumped off. This cycle of operations was repeated until no further evolution of gas took place. The iodine and toluene were degassed in a similar manner.

On completion of these operations, the taps from the circulating system to the vacuum line were closed, traps T_1, T_2, T_3, T_4, T_5 and T_8 immersed in liquid air, T_7 in CO_2-acetone, and T_6 in water at 10°C. The toluene

and iodine reservoirs were immersed in the thermostat baths. When the rate of flow of carrier gas, the furnace temperature, and the thermostat bath temperatures were steady, the injection valves IV.1 and IV.2 were fully opened, and the gas flow directed through the furnace into a spare trap immersed in liquid air. (Not shown in fig.7 but identical with T_7). This served a fourfold purpose:-

a) It allowed the rate of flow of reactants and carrier gas to settle down.

b) Any traces of carrier gas which had leaked into the reactant reservoirs through IV.1 or IV.2 were swept out.

c) Any traces of oxygen in the carrier gas, or any other impurities likely to react with the products were destroyed.

d) Any required pre-conditioning of the furnace surface could be attained.

The gas flow was then directed for an equal time through each of the triplicate sets of traps T_7 etc. by operation of the appropriate solenoid vales SV.2. On completion of the last experiment, the solenoid valve SV.2 was lowered, SV.1 raised, and the reactants plus carrier gas directed for the same time interval through the analysis trap T_4 which condensed out both the toluene and iodine. After the analysis run the gas flow was re-directed through the furnace and into the spare trap.

The reactants were then shut off by closing IV.1 and IV.2 and the circulation of carrier gas continued for two minutes.

In those runs where a hydrogen analysis was also undertaken, tap T_1 was closed and the system evacuated to 10^{-1} mm Hg by means of a Toepler pump backed by the circulating pump. The carrier gas and non

condensible gases were thus compressed into a previously evacuated storage bulb, which could be removed and attached to the gas handling system of a Nier type mass spectrometer for analysis. The circulating pump was then shut off, taps 3, 4 and 6 closed, taps 2 and 5 opened, and the entire collecting system further evacuated through the vacuum line. When this had been completed, taps 2 and 6 were shut and the hydrogen iodide allowed to distil over from T_8 to T_9. Trap T_9 was then allowed to warm up to permit the hydrogen iodide to dissolve in the degassed methanol, the solution then refrozen, T_9 removed, distilled water added and the hydrogen iodide estimated as described previously.

During the time the hydrogen iodide was distilling, a similar fractional distillation was carried out to separate the toluene and iodine in trap T_4; T_5 was immersed in liquid air and T_4 allowed to warm up. This distillation was continued until traces of iodine also appeared in T_5, by which time (as trial experiments had shown) all the toluene had distilled over. The analysis collecting system was then opened to the atmosphere, T_9 detached, and the contents weighed. Methanol was then added and the traces of iodine present estimated by titration with thiosulphate. The total weight of toluene was then corrected for the iodine present. Normally the above correction was insignificant.

The collection and analysis of stilbene has been described previously.

In those experiments in which hydrogen iodide was added to test inhibition, the procedure was slightly different.

a) The analysis run was completed first.

b) The gas flow was then directed through the first of the triplicate trap system. This yielded data on the reaction in the absence of added hydrogen iodide.

c) The gas flow was redirected into the spare trap while the hydrogen iodide injected through K3 reached a steady state.

d) When steady flow conditions had been attained the gas flow was re-routed through the second set of traps.

e) On completion of (d) the gas flow was redirected into the spare trap while the toluene thermostat bath was removed and the reservoir immersed in liquid air. By this means the toluene was shut off without affecting the rate of flow of carrier gas.

f) To allow the input of hydrogen iodide to be measured, the iodine plus hydrogen iodide were passed into the third set of traps. The experiment was then completed in the normal manner.

In this way, the quantities of toluene, iodine and hydrogen iodide injected could be measured and the rate of production of hydrogen iodide in the presence of an added excess of hydrogen iodide contrasted with the normal reaction rate under identical conditions.

EXAMINATION OF SOLID PRODUCTS.

The solid material which condensed out in the U tube T7 from runs done at 945°K melted over the range of 108-115°C. A Lassaigne determination showed the presence of a trace of iodine, possibly absorbed by the solid, and simultaneously condensed out. The material was dissolved in absolute alcohol and recrystallized twice. The material

a) Standard Absorption Spectrum of Pure Stilbene Solvent- Methanol

b) Solid Material from U. Tube.

Slit Width = ·2mm.

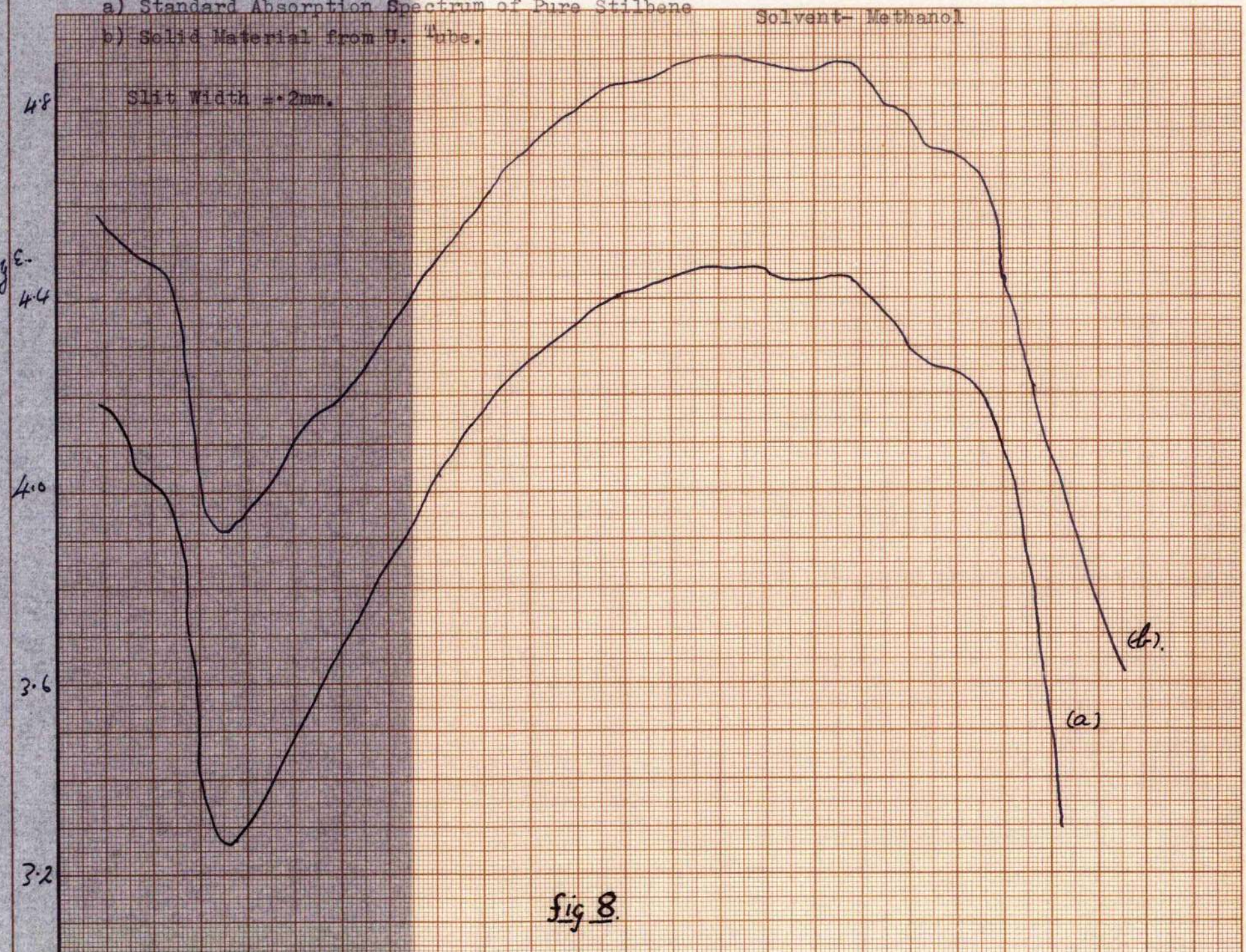


fig 8.

obtained melted sharply at 123.5°C, and a mixed melting point determination with a specimen of pure stilbene showed no depression of the melting point. It was therefore concluded that the major portion of the solid consisted of stilbene.

This was confirmed by the U.V. spectrum of the raw material (fig.8) which is virtually identical with the standard spectrum of stilbene. The slight hump at 250mu suggested the presence of another compound, possibly dibenzyl. Accordingly, a fresh sample of the solid was dissolved in 40-60 petroleum ether (freshly distilled over sodium) and chromatographed on a 1" diameter alumina column, 6" long. The column was developed with a mixture of 4% v/v methanol in petroleum ether, and eluted with

a) a 10% v/v solution of methanol in petroleum ether.

b) methanol alone.

In this manner the material was separated into two fractions;

1) A yellow fraction which fluoresced strongly under U.V. light, and was subsequently rechromatographed four times on fresh columns in an attempt to remove traces of stilbene. The final spectrum obtained is shown in fig.9. The material still contained stilbene and traces of some substance having a fairly symmetrical absorption peak at 250mu. Several substances, notably styrene, diphenyl, and 44' dimethyl diphenyl exhibit a similar absorption in this region. Styrene was ruled out as no peaks were observed at 282 and 292 mu.

Test solutions of diphenyl in methanol failed to exhibit the intense fluorescence of the unknown under U.V. light. The problem of identity of this material was not investigated any further as it made

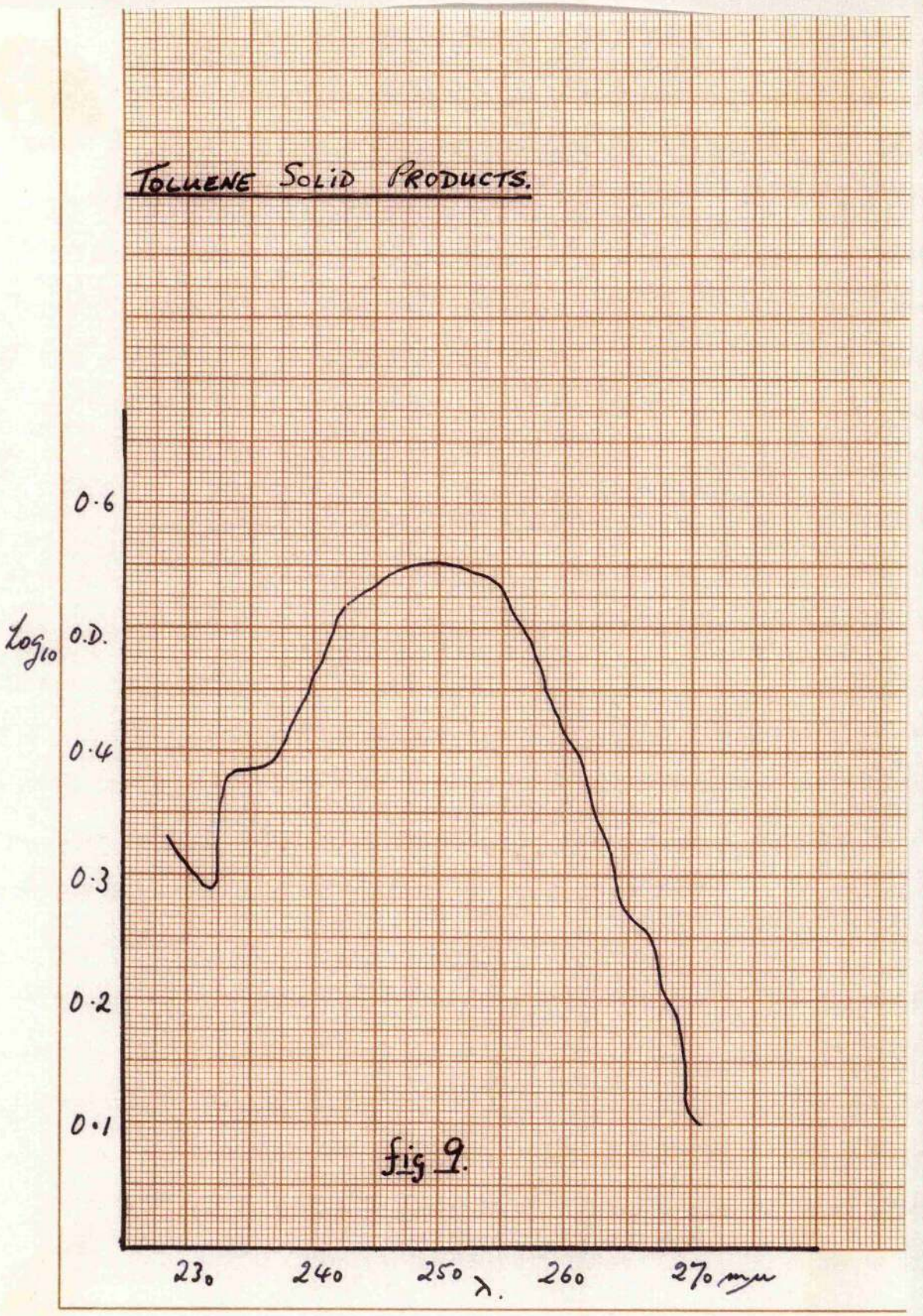

TOLUENE SOLID PRODUCTS.
0·6
0·4
0·3
0·2
0·1
Log10 O.D.
230
240
250
λ.
260
270 mμ

fig 9.

up less than 1% of the total solid and its absorption did not interfere with the accuracy of the stilbene analysis based on the absorption at 318 and 320 mu. The unknown may in fact be 44' dimethyl diphenyl as this compound is stated to be formed in the pyrolysis of toluene. The presence of this material, which has an extinction coefficient of the same order of stilbene, would be quite noticeable after chromatographing the solid to remove most of the stilbene.

2) The second (major) fraction was found to be pure stilbene, M.P.123.5. Dibenzyl (coeff extinction = 10^{+2} at 260 mu) is almost certainly present as well, but its characteristic spectrum would be completely masked by the stilbene. In an attempt to test for its presence, synthetic mixtures containing 3, 6 and 12% by weight of dibenzyl in stilbene were made up, and injected into a mass spectrometer by means of a solid handling system designed by R.N.Pittilo.(78) This consisted essentially of a heated metal valve, similar to I.V.2, connected direct to the mass spectrometer leak together with a detachable reservoir, maintained at 100°C by means of a water bath. Special care was taken in the design of this system to ensure that little or no fractionation of the solid material occurred during analysis. The mass spectrometer was focussed on the 91 peak and the deflection obtained was found to bear an approximately linear relationship to the percentage dibenzyl in the mixture. The solid products of several runs carried out at 945°A were compared with the synthetic mixtures and found to contain some 3-8% dibenzyl.

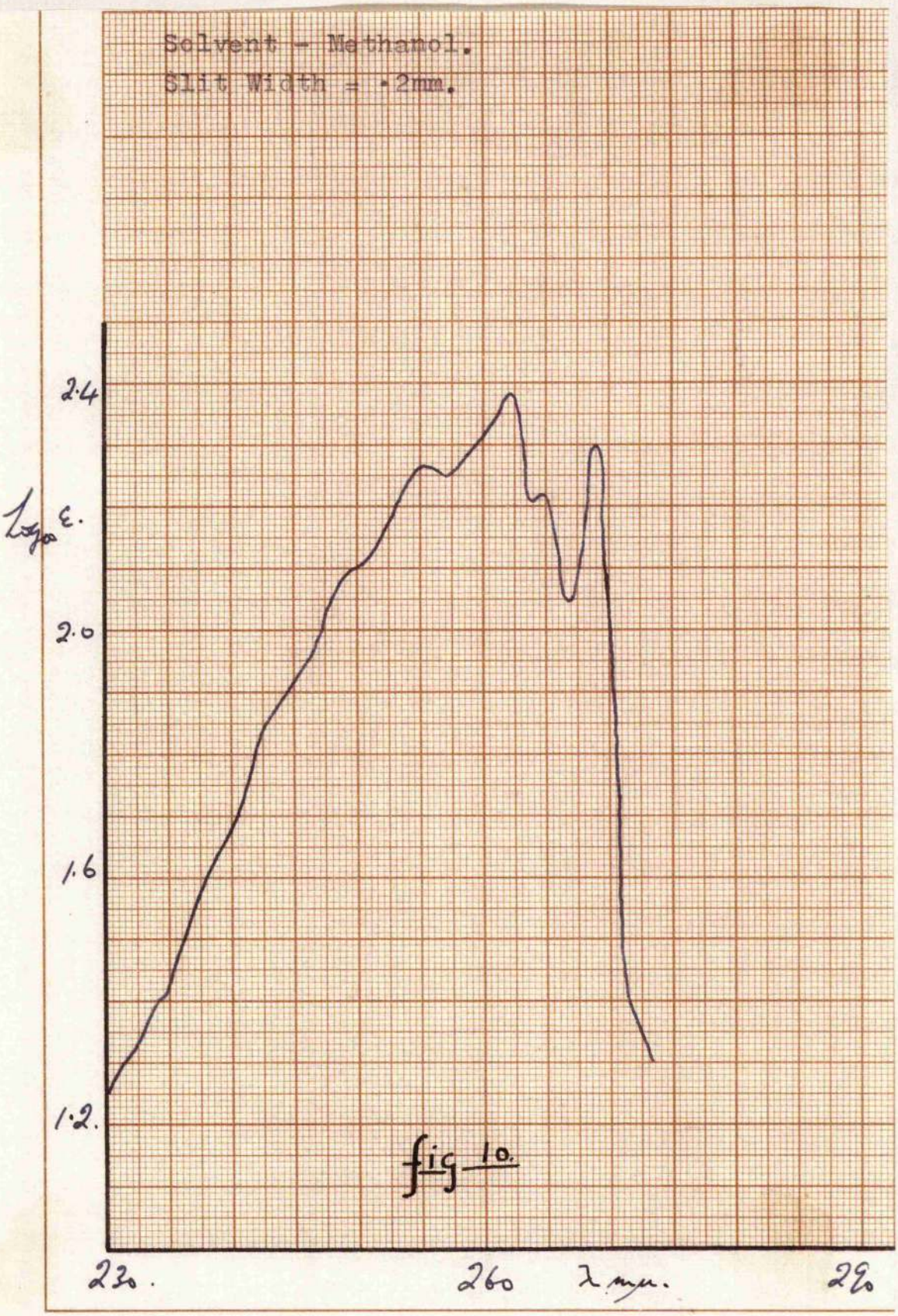

Solvent - Methanol.
Slit Width = ·2mm.
2·4
log ε.
2·0
1·6
1·2.
230.
260
λ mμ.
290

fig 10.

PRODUCTS FROZEN OUT AT -80°C IN T.7.

The organic material condensed out with the iodine in the -80°C trap was allowed to distil over into a receiver immersed in liquid air. After two further vacuum distillations, a clear liquid was obtained. The U.V. spectrum (fig. 10) of this material showed that it consisted entirely of toluene. No peaks were observed at 282, and 292mu indicative of styrene, which might have been obtained from the direct decomposition of toluene or dibenzyl, and apart from undecomposed toluene no other volatile organic material was found.

In order to test whether any non volatile organic components had condensed out in the -80°C traps, the iodine in a second trap was destroyed with excess concentrated thiosulphate, the organic material extracted with chloroform, the chloroform subsequently evaporated off, and the residue dissolved in methanol. In this instance (fig.11) the toluene spectrum is masked by traces of stilbene which have passed through the U. tube T_6; even so no other substance appears to be present.

Before a complete analysis of the toluene results could be attempted it was thought advisable to investigate the production of stilbene from the reaction between dibenzyl and iodine.

It had been assumed in previous discussions that the production of stilbene was accompanied by the formation of two molecules of hydrogen iodide. The only other product, hydrogen, could be partially accounted for by the $\approx$ 1% decomposition of toluene, which according to Steacie would be expected at these temperatures. A search of the literature revealed that no comparable gas phase investigation had so far been attempted with dibenzyl and iodine.

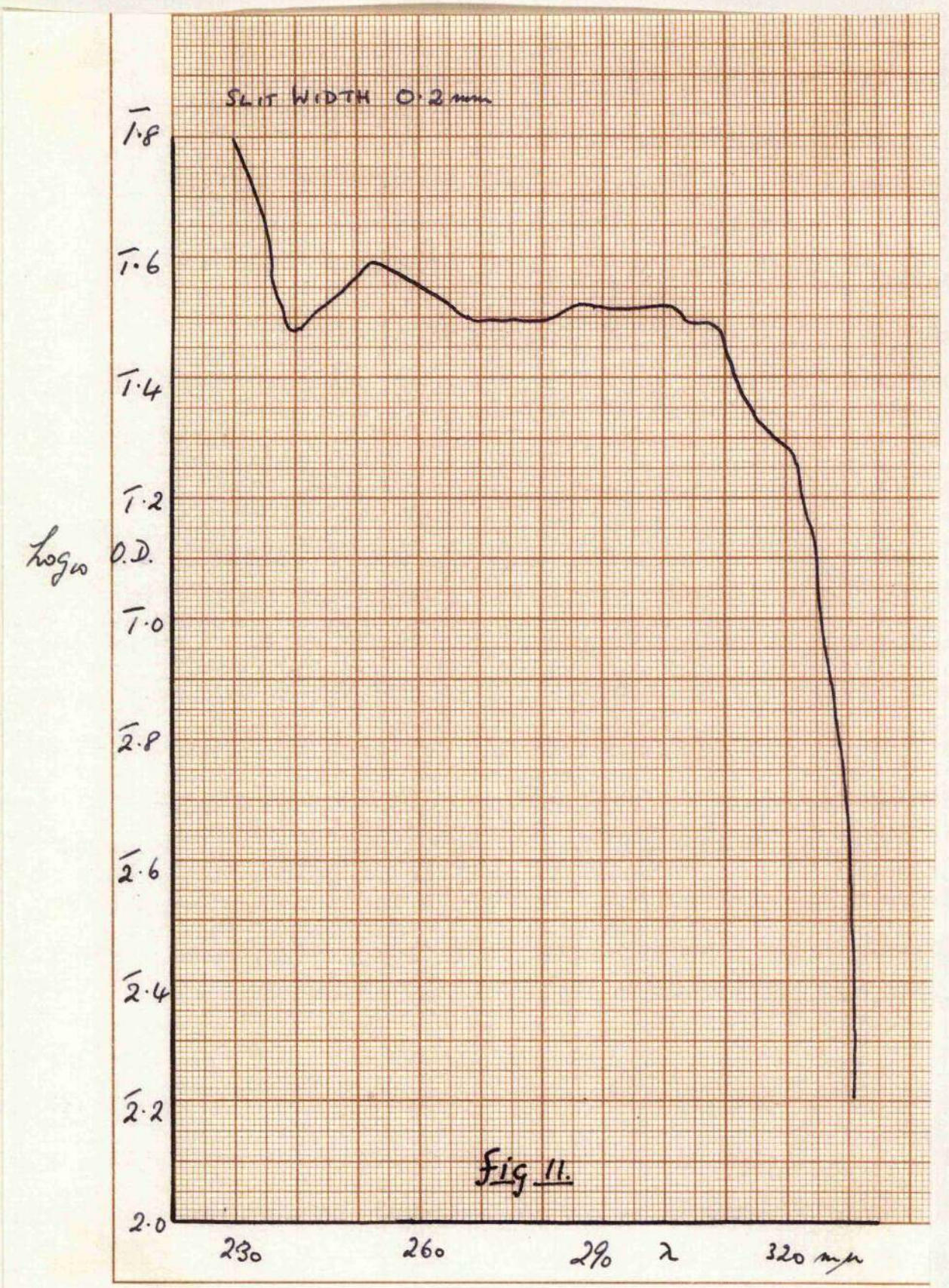

SLIT WIDTH 0·2 mm
$\bar{1}\cdot8$
$\bar{1}\cdot6$
$\bar{1}\cdot4$
$\bar{1}\cdot2$
$\log_{10}$ O.D.
$\bar{1}\cdot0$
$\bar{2}\cdot8$
$\bar{2}\cdot6$
$\bar{2}\cdot4$
$\bar{2}\cdot2$
2·0
230
260
290
λ
320 mμ

Fig 11.

THE REACTION BETWEEN DIBENZYL AND IODINE.

The pyrolysis of dibenzyl and iodine was carried out in the same apparatus used for the pyrolysis of toluene and iodine.

The dibenzyl was injected into the system by means of the toluene valve I.V.2 which was maintained at 200°C. A sufficient rate of flow of dibenzyl was obtained, (without altering the capillary inside the valve), by raising the temperature of the reservoir bath to 140°C. This was quite simply accomplished by raising the power input to the heater, and making the necessary adjustments to the thermostat. Due to the relatively low vapour pressure of dibenzyl, the original furnace input and output heaters were boosted up so that they maintained the associated glass ware at approximately 80°C. At this temperature the Edwards W.E.6 wax becomes plastic, but still retains sufficient rigidity to form vacuum tight joints between the silica furnace and the rest of the apparatus.

The input heater was extended so that it covered the entire double solenoid valve S.V.1., and all the input line (including the hydrogen iodide injection capillary K3) between the injection valve I.V.1 and the furnace.

In addition to these modifications, a simple U tube (not shown in fig.7, but identical with T_6 at the furnace exit) was inserted between SV.1 and T_4. The input to this U tube from SV.1 was also heated to 80°C by means of nichrome tape. Apart from this U tube the apparatus was therefore virtually the same as that used for the study of toluene and iodine.

U.V. SPECTRUM OF DIBENZYL IN METHANOL.

CONCENTRATION = ·4855 grms / litre.

= 2.66×10^{-3} gm mols / litre.

% Stilbene = ·25%

ε_{260} DIBENZYL = 4.21×10^{2}.

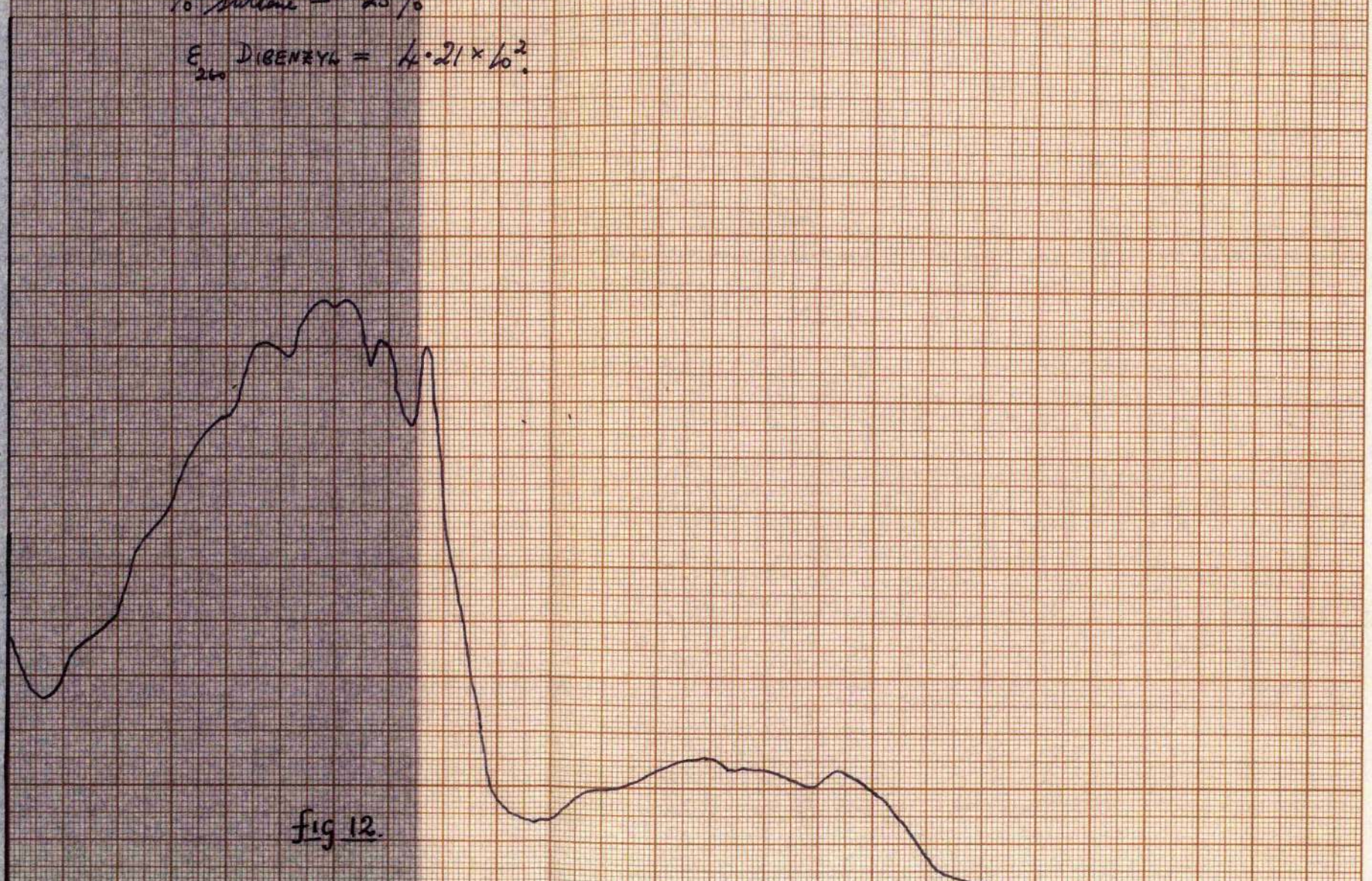


Fig 12.

Reactants.

Iodine. The iodine used was taken from the same stock prepared for the pyrolysis of toluene.

Dibenzyl. Commercial dibenzyl supplied by B.D.H. was purified by several crystallizations from absolute alcohol. Although this product melted quite sharply at 52°C, its U.V. absorption curve showed on comparison with that given in the American Petroleum Institute catalogue of UV data that the material still contained some 2 to 4% stilbene which almost masked the characteristic absorption spectrum due to dibenzyl. In an attempt to remove this impurity, the material was redissolved in absolute alcohol and refluxed with ten times the theoretical quantity of sodium required for the reduction of the stilbene present. By repeating this procedure five times and examining the absorption curves of the product obtained from each reduction it was found that reduction under these conditions could remove all but 2% of the stilbene.

The material obtained from these reductions was then dissolved in amyl alcohol (B.P.130°C) and refluxed for 30 minutes with excess sodium. On the completion of the reaction the amyl alcohol was distilled off, and the product recrystallized from absolute alcohol. The absorption curve for this material showed that it contained less than 1% stilbene (M.P.52.5°C).

The above reduction was repeated a second time on a small fraction of the material and yielded a specimen of dibenzyl containing about 0.25% stilbene (M.P.52.5°C). The absorption spectrum for this material is shown in fig.12. In the initial runs this relatively pure material was used, but when it became obvious that the conversion of dibenzyl to stilbene was going nearly to completion, the dibenzyl containing 1% stilbene was

used instead, and, where significant, the 1% impurity was allowed for in the calculations.

GENERAL DESCRIPTION OF AN EXPERIMENT.

The precautions observed in the operation of the apparatus in the reaction of toluene and iodine were observed in the reaction of dibenzyl and iodine.

During each run, the U tube T_6 was maintained at 10°C. This collected all the stilbene as previously but allowed the iodine to pass through to trap T_7, which was immersed in CO_2 - acetone mixture at -80°C. Trap T_8 was immersed in liquid air to condense out the hydrogen iodide formed. (See fig. 7).

The method of collection and estimation of the reactants passing into the furnace differed slightly from that used with toluene. Trial runs using dibenzyl showed that with the very small partial pressures of dibenzyl employed (circa 10^{-2} mmHg, approximately same as would be formed during the runs with toluene) appreciable quantities would pass through a U tube held at 10°C. In point of fact, in order to ensure the complete collection of the dibenzyl, the U tube would have to be immersed in liquid air. If iodine were simultaneously flowing in the system then it also would be removed. A trial run showed that the rate of flow of gas, and the rate of injection of dibenzyl remained unaltered even if the iodine was shut off by replacing the iodine reservoir bath with a dewar vessel containing liquid air. Accordingly, during an experiment, the

Table 10.

All concentrations moles x 10^{-7} / litre.

Run No.	T°K	Contact Time seconds.	(DB) IN	(I_2) IN	(HI) Exit.	(St.) Exit.	(HI)/(St.)
289	898	0.246	11.09	9.0	6.02	4.84	1.25
290	898	0.246	11.09	9.37	6.58	4.84	1.36
291	898	0.246	11.09	9.36	7.17	4.84	1.48
292	810	0.280	3.90	11.72	1.86	1.99	0.94
293	810	0.280	3.90	12.1	1.95	1.99	1.00
294	810	0.280	3.90	12.1	2.06	1.99	1.03
295	851	0.267	2.63	12.1	0.80	1.06	0.75
296	851	0.267	2.63	12.24	0.80	1.06	0.75
297	851	0.267	2.63	12.37	0.87	1.06	0.82
301	945	0.247	11.34	9.06	2.82	7.55	0.37
302	945	0.247	11.34	9.91	3.00	7.55	0.40
303	945	0.247	11.34	10.06	3.08	7.55	0.41

301 - 303 Hydrogen analysis 0.18 x 10^{-7} moles/litre.

apparatus was allowed to reach a steady state by running the products formed (for a noted time interval) into a spare trap immersed in liquid air.

When equilibrium conditions of flow had been reached the gas flow was directed for a given time through each set of traps in the triplicate collection system. On completion of the reaction, the gas flow was again directed through the spare trap while the oil bath was removed from the iodine container and replaced by the liquid air. A minute was sufficient to cut off the flow of iodine completely and the carrier gas plus dibenzyl was then directed by means of the double solenoid valve S.V.1 through the analysis U tube and trap T_4. On completion of the analysis run the gas flow was again passed through the spare trap, the dibenzyl cut off by closing IV.2, trap T_6 immersed in acetone - CO_2, and the apparatus evacuated through taps 2, 5, and 12.

In those experiments in which the quantity of hydrogen formed was estimated the procedure was identical with that used in the pyrolysis of toluene.

The procedure for the collection and estimation of hydrogen iodide and iodine in traps T_8 and T_7 has also been discussed previously (see page 56). The input concentration of iodine was estimated as the sum of the residual unattacked iodine plus that converted into hydrogen iodide. A specimen of the calculations involved is given later.

Table (10) shows the experimental results obtained over the temperature range 809 - 945°K. These results clearly show:

a) that the formation of stilbene is accompanied by the formation of a variable amount of hydrogen iodide and not the ratio of 2 moles hydrogen iodide to 1 mole stilbene.

b) at 945°K the dibenzyl is nearly all converted to stilbene, but only 50% conversion takes place at 809°K.

c) the quantity of hydrogen formed is only a twentieth of the amount of hydrogen iodide, and appears to be roughly in the same proportion as found in the toluene pyrolysis. It would therefore seem that nearly all the hydrogen found in the toluene pyrolysis was formed in this secondary reaction.

EXAMINATION OF SOLID PRODUCTS.

At this point a further examination of the products obtained in the U tube T6 and in the -80°C trap T_7 seemed desirable. During the analysis of the iodine found in traps T_7, small drops of an organic liquid were noticed adhering to the walls of the trap. A further quantity of the material seemed to condense out with the hydrogen iodide in trap T_8. The liquid itself smelt strongly of toluene, and seemed to possess a similar volatility.

After titration of the iodine with thiosulphate, the organic material was extracted with chloroform, the chloroform washed, dried, and then distilled off. The residual material on cooling, deposited a few crystals (the traces of dibenzyl which passed through trap T_6 and condensed out here) but did not itself crystallize. The material was then reheated in an attempt to distil off any toluene or other volatiles, but it decomposed below 100°C and before any further

b) Spectrum of Oily Deposit in 'Cardice' Trap. (-80°c).

Solvent - N Hexane. a) Toluene.

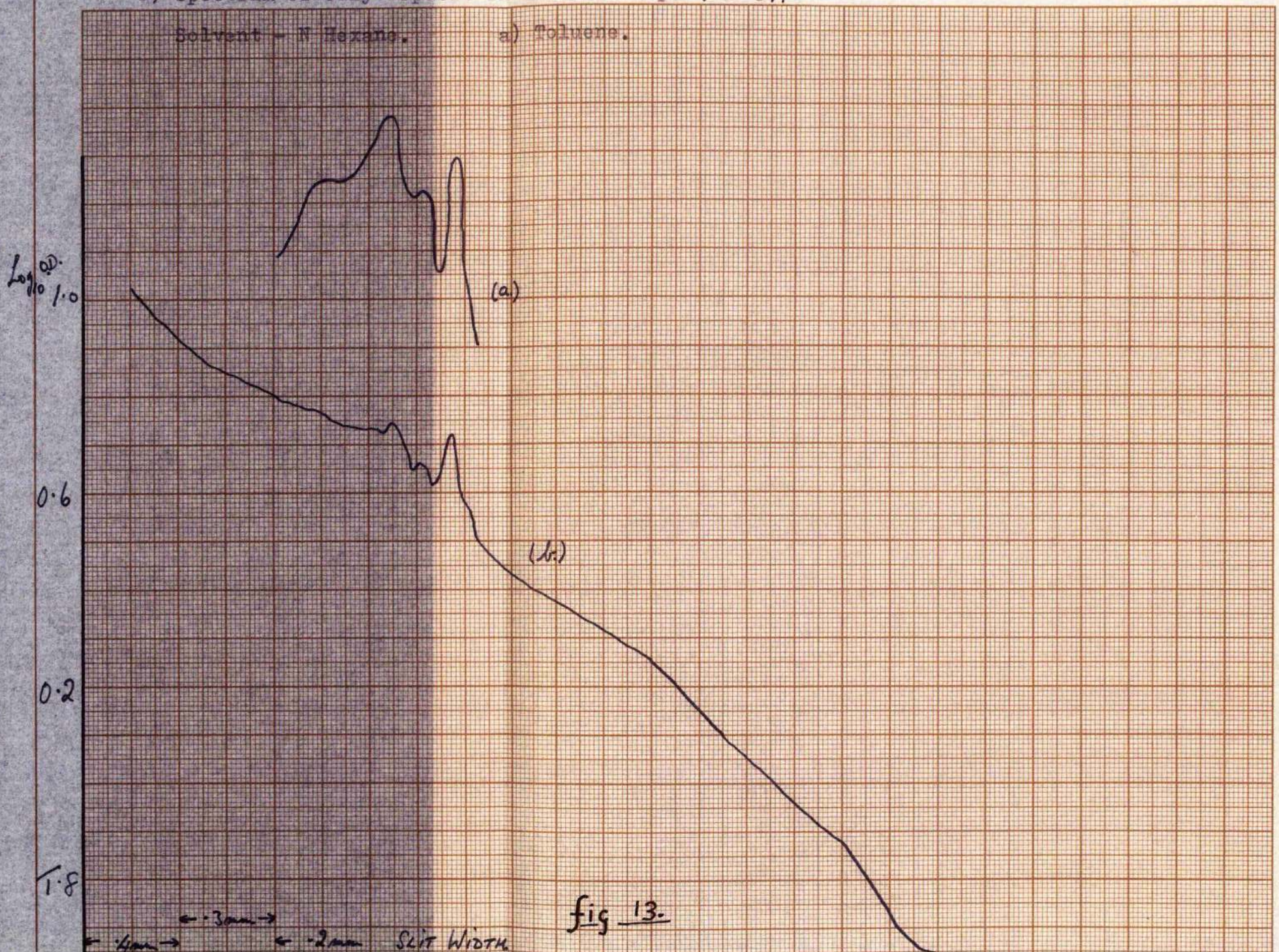


fig 13.

distillation took place liberating a small quantity of iodine, and traces of hydrogen iodide.

The tarry oil remaining was dissolved in a little chloroform, and passed through a small chromatographic column, containing aluminium oxide, to remove the tar. The column was then eluted with methyl alcohol and the combined extracts injected into the gas handling system of a mass spectrometer. A scan of the peaks of mass number 80 - 93 showed that the 91 and 92 peaks had increased. The increase showed the presence of toluene and possibly in the case of the 91 peak, dibenzyl.

In order to test the effect of dibenzyl dissolved in a toluene sample, equal quantities of toluene, and a synthetic mixture consisting of 80% by weight of dibenzyl in toluene were injected into the gas handling system by means of a micro-pipette, capable of delivering accurately 0.001ml. of liquid. These tests conclusively proved that in the gas system used the dibenzyl dissolved in the toluene exerted insufficient vapour pressure to affect the toluene mass spectrum.

Further proof of the presence of toluene was afforded by a fresh sample of the oily product which was dissolved in spectroscopic quality (B.D.H.) n-hexane and subjected to U.V. examination. The absorption curve is shown in fig. 13. The uniform background rise in absorption is characteristic of an organic iodide thus confirming the above observations.

Superimposed on this background absorption are three peaks at262, 265, and 269mu, corresponding with the standard toluene spectrum (inset) and clearly not due to dibenzyl which shows maximum peaks of absorption at 259, 264, and 268mu.

Further experiments were undertaken in an attempt to find out the approximate ratio of toluene to the other products. In order to do this the experimental procedure was modified slightly. Only two sets of the triplicate trap system were used in the conventional manner for the collection of iodine and hydrogen iodide. Trap T_7 of the third set was immersed in liquid air instead of solid CO_2 and all the volatile products were collected in this trap.

At the end of an experiment trap T_7 was removed and filled with a concentrated thiosulphate solution to destroy the iodine and hydrogen iodide. The resultant solution was then extracted with n-hexane and analysed on the U.V. spectrometer. However the background absorption rendered accurate analysis impossible and the project was abandoned in order to investigate the reaction between dibenzyl and hydrogen iodide.

TABLE (11).

Fraction.	Melting Range.	Compound.
1	50 - 55°C	Dibenzyl
2	121 - 123°C	Stilbene
3	15 - 20°C	Dimethyl diphenyls
4	oil	Not known

EXAMINATION OF THE U TUBE (T_6) PRODUCTS.

The U tube products obtained after several hours continuous operation were dissolved in sodium dried petroleum ether and passed through a 1" diameter column of alumina 6" long. The column was eluted with petroleum ether until no further material passed through, by which time three apparently clear cut fractions had been collected.

Examination of the column under U.V. light from a Hanovia lamp showed a clear cut fluorescent band at the top of the column. This band appeared to contain a yellow material in normal daylight, and a similar band had been observed previously when chromatographing the solid products from the toluene pyrolysis. The column was allowed to dry completely, it was then cut up, and the portion containing the fluorescent material dissolved in spectroscopically pure methanol. Each of the three fractions was evaporated to dryness on a water bath, and the solid residue dissolved in methanol. The corresponding absorption curves obtained for each fraction are shown in fig. 14.

On completion of the U.V. examination the solutions were again evaporated to dryness, and, where sufficient residue remained, the melting point of each was determined using a hot stage microscope. The melting points are listed in table (11), along with those of possible compounds giving rise to the spectra.

On evaporation or on standing, fraction two developed a slight reddish tinge due to the presence of an unstable iodide. (Possibly an addition compound of stilbene with iodine). In spite

Spectra of Fractions Obtained from Chromatographic Column.

Solvent - Methanol. Slit Width = ·2mm.

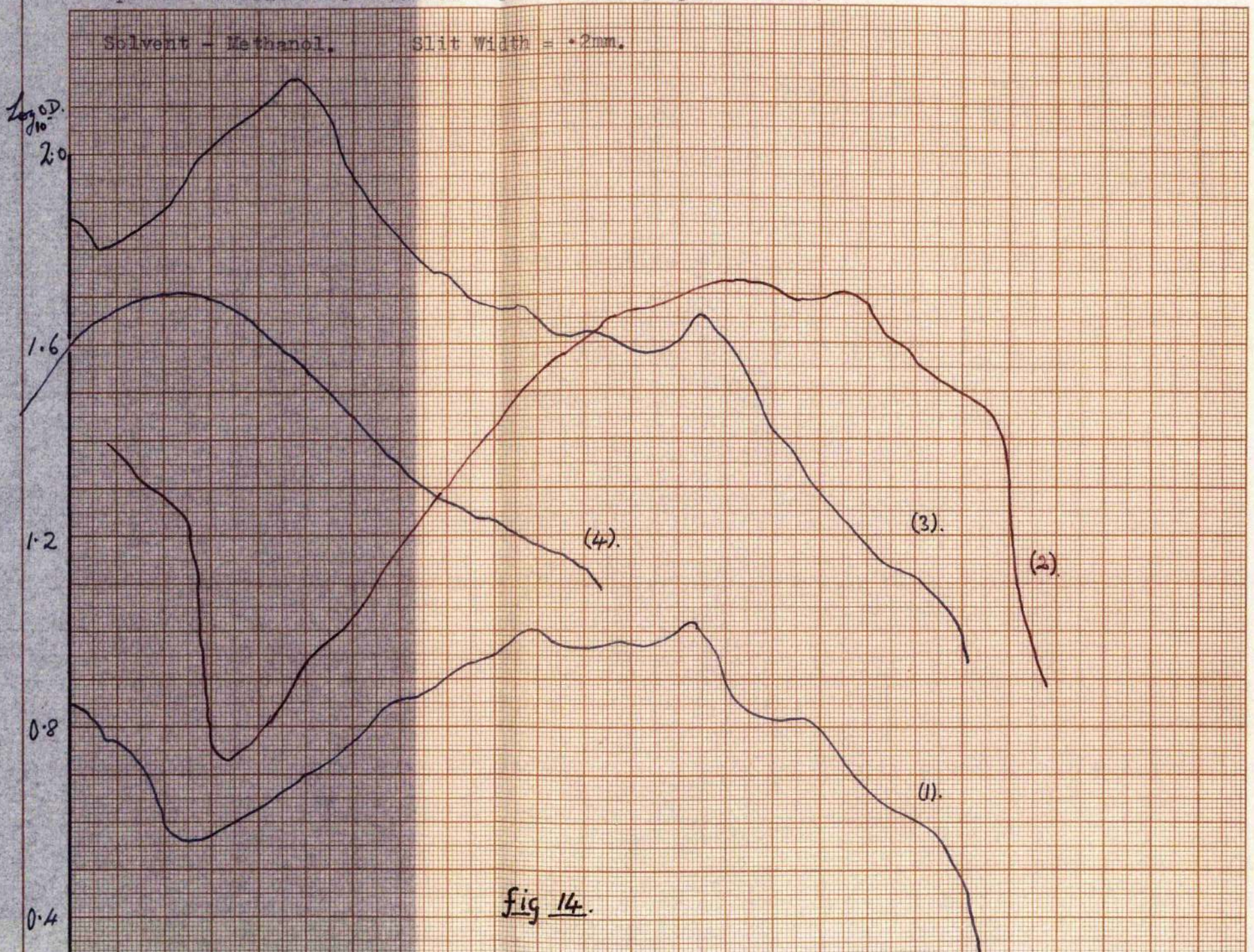


Fig 14.

of this, the spectrum of fraction two was found to be identical with that of stilbene. This fraction was the largest and made up the major portion > 99% of the solid products.

The other fractions yielded only two to three mg of solid on evaporation.

The spectrum from fraction one is also quite similar to that for pure stilbene, and although there was too little material available to allow the melting point to be determined with the hot stage microscope, it was observed that the traces of solid left on the flask after evaporation melted in the region 50-55°C. This fraction was presumably mainly dibenzyl, the presence of a few percent stilbene completely masking the dibenzyl spectrum. (The slight peak in the absorption curves at 296mu is possibly due to an impurity in the petroleum ether as it seems to be present in all the spectra).

The U.V. spectrum of fraction three shows an interesting hump at 253mu. This may be due to a mixture of dimethyl diphenyls. Steacie[72] in his paper on the pyrolysis of toluene reported that moist crystals were obtained from his chromatogram which yielded a spectrum similar to this, and which he attributed to the presence of a mixture of 33', 34, and 34' dimethyl diphenyls. The fraction melted over a reasonable range of temperature for such a mixture.

The fluorescent ring on the column yielded on evaporation a yellow repulsive smelling oil. The absorption curve for this material is also shown in fig. 14(4). The spectrum consists of a symmetrical

hump between 230 and 252mu the peak being reached at 242mu. The origin of spectrum 4 is unknown. The yellow colour suggested traces of mercuric iodide might be present, but according to Lederie[89] and others if HgI_2 were present in sufficient amount to contribute to this absorption, then a similar peak would exist at 272mu. No such peak was observed. At any rate any peak in this region due to HgI_2 would reach its maximum at 214mu, and this would seem to rule out the presence of HgI_2. Likewise, although the spectrum of another possible compound, diphenyl, is very similar to (4) the peak occurs at 246mu and not 242mu. In any case it seems unlikely that diphenyl would be more strongly absorbed on to alumina than stilbene. Moreover diphenyl is a solid, M.P. 67°C, whereas the fraction was an oil. It would seem that the spectrum is due to an unknown substance which is in all probability more unsaturated than stilbene, is a yellow coloured liquid at room temperature, and exhibits a brilliant blue fluorescent effect under U.V. light.

As stated above, the solid products consisted of about 99% stilbene, and, as none of the other spectra absorbed at wavelengths greater than 300mu, reliance could be placed on the accuracy of the analysis for stilbene based on the assumption that at 314, 318 and 320mu, the absorption could be ascribed to the presence of stilbene alone.

From the above analysis it would appear that the main products from the reaction between dibenzyl and iodine are hydrogen iodide, stilbene, and toluene. The presence of toluene in quantities much

greater than would be expected from the decomposition of dibenzyl by itself in the absence of hydrogen iodide or iodine suggested that benzyl radicals were attacking the hydrogen iodide produced by the reaction between dibenzyl and iodine. This idea was further supported by the high ratio of stilbene to hydrogen iodide produced. Provided the formation of one molecule of stilbene was accompanied by two moles of hydrogen iodide, there seemed to be no other manner in which the hydrogen iodide could be destroyed without the formation of a much larger quantity of molecular hydrogen than actually appeared. In fact the amount of molecular hydrogen (H_2) actually found (1.62×10^{-7} moles/litre) was more probably due to the decomposition of the hydrogen iodide itself ($\approx$ 3% at this temperature).

Accordingly, further consideration of these results was deferred until the possibilities of the reaction between dibenzyl and hydrogen iodide had been investigated.

Dibenzyl and Hydrogen Iodide.

Experimental Technique.

No modifications were necessary to the apparatus, and the experimental techniques used to inject and analyse for dibenzyl and hydrogen iodide have already been described in previous experimental sections.

Examination of products in trap T.7.

After a lengthy run all the products were collected in trap T 7, on this occasion at $-184^{\circ}C$, and the organic material together with hydrogen iodide distilled over into a removable side arm containing

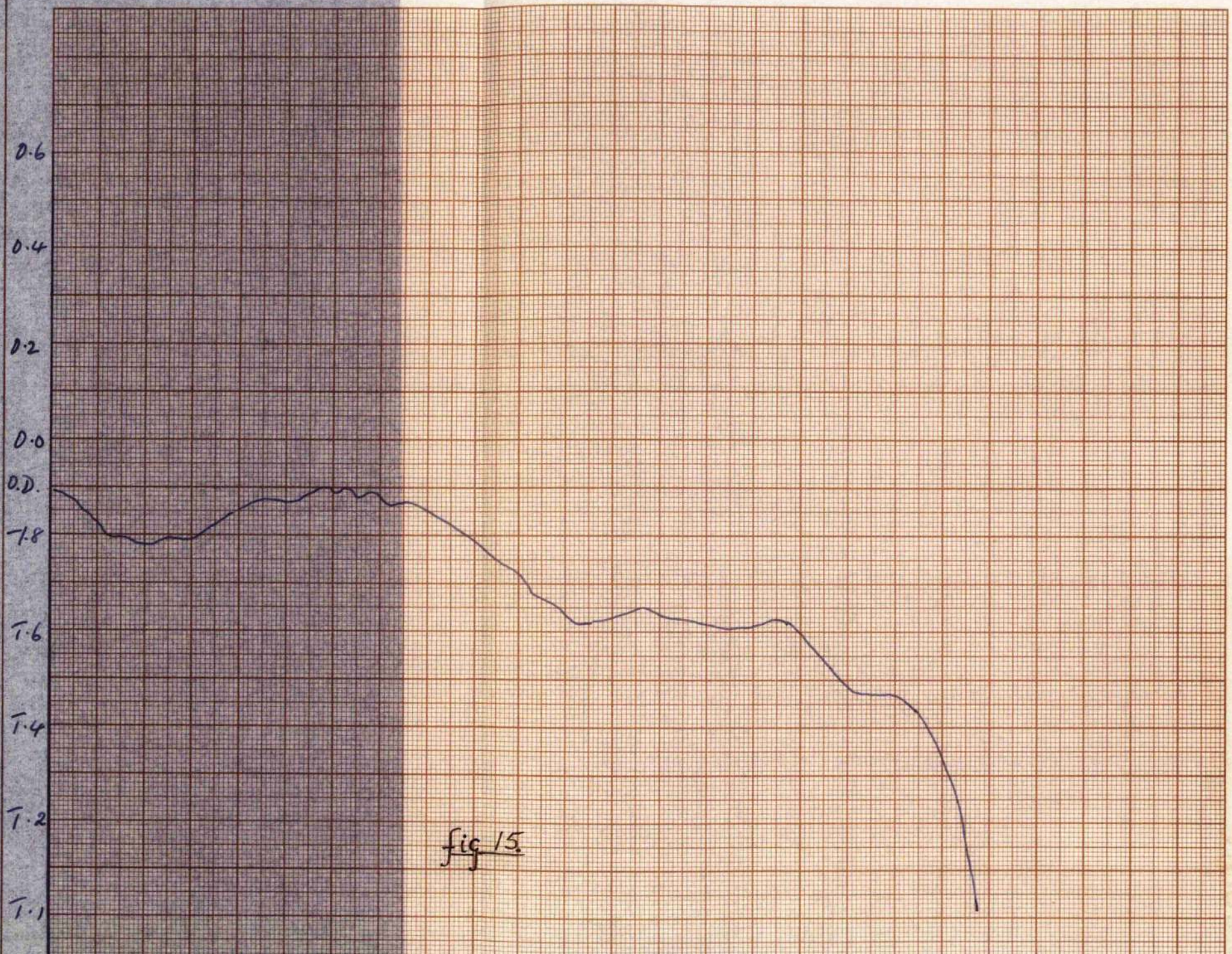


fig 15.

methanol, which was subsequently detached and all the hydrogen iodide allowed to evaporate off.

The organic liquid obtained smelt strongly of toluene, however. U.V. analysis of this solution showed that the spectrum of stilbene was predominant (fig.15). This was expected for some traces of stilbene would always pass through the U tube T 6 and be carried over with the toluene during the low temperature distillation. The presence of toluene was confirmed by mass spectroscopic analysis of the solution and the quantity obtained shown to be almost equivalent to the amount of iodine atoms formed (in fact 90% of the quantity theoretically expected from the equation)

$$C_7H_7\cdot + HI \longrightarrow C_7H_8 + I\cdot$$

No other organic products were detected but the presence of toluene was further confirmed by subjecting a second batch of products collected in the manner given above to a low temperature distillation into an empty receiver followed by a normal microdistillation at atmospheric pressure. The small quantity of organic liquid obtained on solution in methanol yielded a U.V. spectrum identical with that of pure toluene.

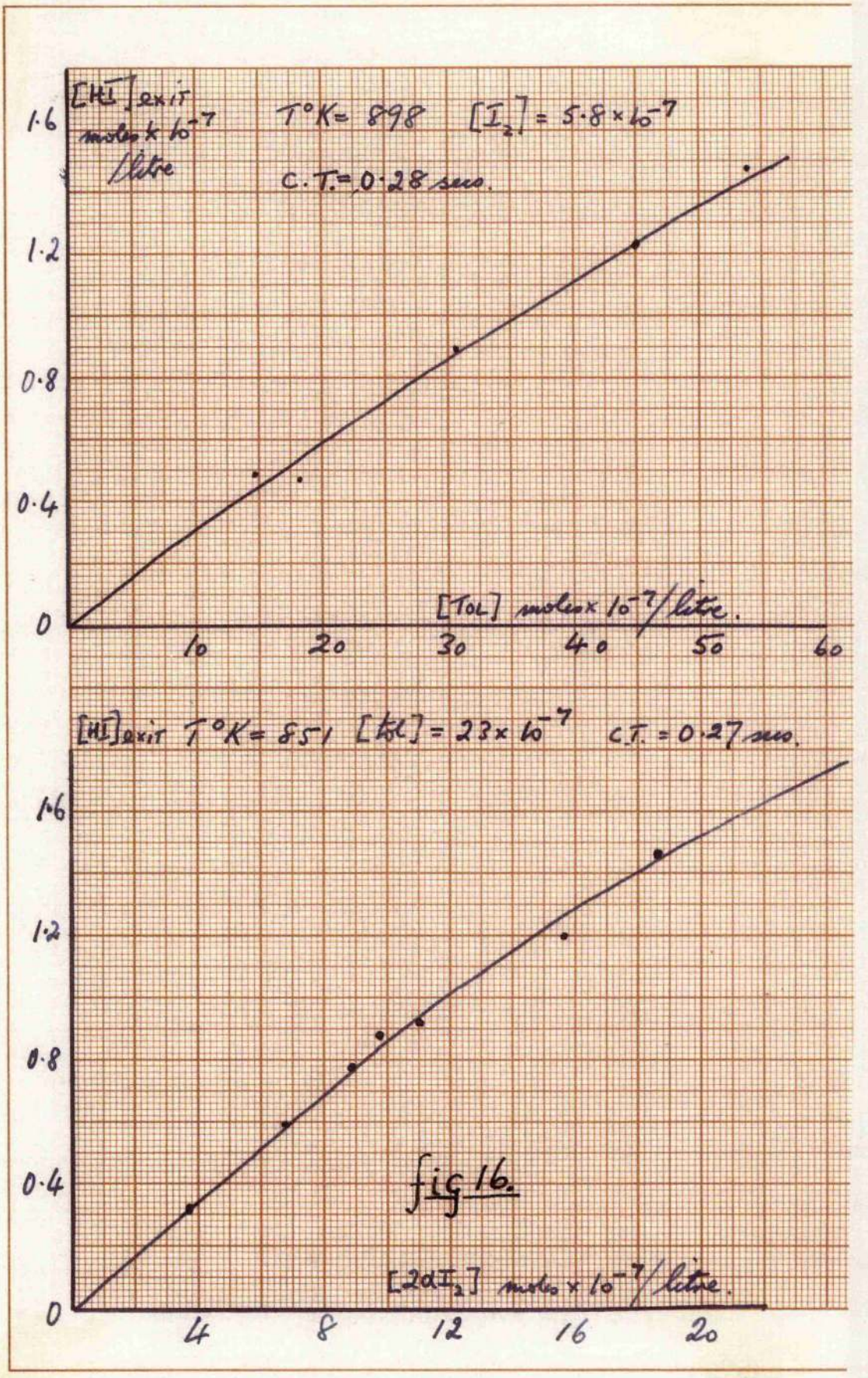

[HI]exit moles × 10⁻⁷ / litre
T°K = 898 [I₂] = 5·8 × 10⁻⁷
C.T. = 0·28 secs.
1·6
1·2
0·8
0·4
0
[TOL] moles × 10⁻⁷ / litre.
10
20
30
40
50
60
[HI]exit T°K = 851 [TOL] = 23 × 10⁻⁷ C.T. = 0·27 secs.
1·6
1·2
0·8
0·4
0
[2dI₂] moles × 10⁻⁷ / litre.
4
8
12
16
20

fig 16.

Discussion of qualitative experimental results and formulation of general reaction scheme.

Reaction of toluene and iodine.

(a) Effect of reactant concentrations.

In the preliminary investigation of the reaction between toluene and iodine analysis was confined to estimating the toluene and iodine input and the quantity of hydrogen iodide produced. Estimations of the extent of the reaction based on the total hydrogen iodide produced showed that (table (12)) considerable reaction had occurred at the temperatures and contact times selected. At this stage no attempt was made to identify and estimate the traces of solid products at the furnace exit.

Table (12).

Toluene and Iodine. All concentrations moles x 10^{-7}/litre.

P_{N2} = 3.9 mm. (I) = Total iodine input as grm atoms.

No.	$T^{o}K$	Contact time. Seconds.	(Toluene) IN	(I_2) IN	(HI) exit	$\%\frac{(HI)}{(Tol)}$	$\%\frac{(HI)}{(I)}$
92	874	0.26	21.9	5.44	1.090	5.0	10.0
98	864.5	0.26	21.8	4.94	0.725	3.3	7.3
106	827	0.27	23.9	7.7	0.599	2.5	3.9
131	944	0.24	23.7	6.6	3.420	10.2	22.0

The dependence of hydrogen iodide production on the toluene and iodine atom concentrations is also shown in fig. (16). In neither case was a strict linear relationship obtained. A threefold increase in toluene concentration shows a proportional increase in the hydrogen iodide at the exit. In fig.(16) the output concentration of hydrogen iodide is plotted against twice the product of the mean iodine concentration

and α the fraction of it which is dissociated at the temperature of the experiment. (See Appendix (6) for the derivation of α).

The amount of hydrogen iodide issuing from the reactor appears to be proportioned to the iodine atom concentration expressed as $2\alpha(I_2)$ with a fall off in the proportionality at higher iodine concentrations indicating possible inhibition.

In order to test whether the actual rate of dissociation of iodine would have any effect on the experimentally measured reaction rate, the half life period for the dissociation process was calculated for various temperatures, assuming a first order rate constant and the value E = 35.5 K. cals/mol for the activation energy. (Table (13)). Under the conditions selected the half life period for the dissociation of iodine is approximately 10^{-5} seconds.

Table (13).

Dissociation of Iodine.

$K\ (sec^{-1}) = 10^{13} \exp\ (-E/RT)$. Half life period = $T_{1/2} = 0.69/K$

T^oK	809	851	898	921	945
$K(sec^{-1}) \times 10^{-4}$	0.25	0.72	2.20	3.60	5.90
$T_{1/2}$ sec $\times 10^5$	28.0	9.60	3.14	1.90	1.17

The correlation between hydrogen iodide production and mean iodine atom concentration shown by fig(16) appears at first sight to be an adequate indication that the reaction proceeds by an atomic mechanism. It must however be pointed out that the values of α appropriate to these experiments are high and in many cases exceed 0.9. (See Appendix (6)).

It would have been more satisfactory to have worked in a lower temperature region, where the classical proof of atomic reactions- a rate proportional to the square root of the iodine concentration - might be attained. However, as previously mentioned, the lower temperature limit was fixed at 800°K, above which, according to Szwarc, any benzyl iodide formed would instantly decompose. The presence of this compound in the products would have greatly complicated the analysis.

(b) Inhibition by Hydrogen Iodide.

The indicated evidence for inhibition was later tested by injecting a third component, hydrogen iodide into the gas stream. In spite of the very considerable technical difficulties involved in controlling the simultaneous injection of three separate reactants into the flow of carrier gas, the results listed in table (14) definitely confirm that Hydrogen iodide does exhibit an inhibiting effect on the extent of its own production.

Table (14)

Hydrogen Iodide Inhibition.

Toluene and Iodine. All concentrations moles X 10^{-7} litre.

Temps 945°K Contact Time 0.23 secs. $P(N_2)$ = 3.9 mm.

No.	Toluene IN	(I_2) IN	(HI) IN	(HI) EXIT	(HI) FORMED
271	4.08	17.2	0	1.353	1.353
272	3.95	16.6	2.56	3.234	0.674
283	19.8	11.7	0	4.04	4.04
284	19.0	12.1	5.35	6.89	1.54
280	40.9	21.2	0	8.91	8.91
281	40.1	20.8	4.04	10.80	6.76

(c) Tentative Reaction Scheme.

The isolation and identification of stilbene as the major solid product together with small quantities of dibenzyl has already been mentioned in the section on product analysis. This together with the evidence of hydrogen iodide inhibition suggested the following reaction scheme:- Fig.(17).

$$2\,C_7H_8 + 2I \underset{2}{\overset{1}{\rightleftharpoons}} 2C_6H_5CH_2^{\cdot} + 2HI$$

$$2C_6H_5CH_2^{\cdot} \underset{4}{\overset{3}{\rightleftharpoons}} C_6H_5.CH_2-CH_2.C_6H_5$$

$$C_6H_5.CH_2-CH_2.C_6H_5 \xrightarrow{5} C_6H_5.CH=CH.C_6H_5 + 2HI$$

fig (17)

The lines of evidence for (1) and (2) have already been indicated, while (3) would be the obvious source of dibenzyl. Moreover if the (C -H) bond in toluene can be attacked by iodine atoms, then the central (C-H) bonds in dibenzyl would be expected to be susceptible to attack also at these temperatures, thus making (5) a reasonable prediction. This is also supported by the experimental evidence at 945°K where the ratio of hydrogen iodide produced to stilbene approaches the theoretical ratio of 4:1 assuming all the toluene attack is converted into stilbene. (Table 15).

Table (15).

Toluene and Iodine All concentrations moles X 10^{-7}/litre $P(N_2)$ 3.9 mm.

No.	T°K	Toluene IN	(I_2) IN	(HI) EXIT	(St) EXIT	(HI)/(St)
158	927	22.2	8.39	2.59	0.69	3.9
166	939	41.8	8.99	5.78	1.24	4.66
191	945	51.8	12.67	8.67	2.07	4.19
197	963	32.8	5.16	2.84	0.67	4.23

The consideration of (4) as a possibility arose when plans for further investigations were being formulated on the basis of this scheme. It was clear that (5) could be made the subject of direct tests, the results of which are discussed later.

The central bond in dibenzyl is expected to be weaker than a normal (C—C) bond and at the outset of this work a value of its bond dissociation energy in the neighbourhood of 50 K.cal.was considered possible. Therefore at 898°K, assuming a normal first order behaviour and velocity constant $k = 10^{13} \exp(-50000/RT)$, we obtain a half life of 0.11 seconds. It was therefore thought worth while to include (4) as a subject for test by studying the reaction of dibenzyl with hydrogen iodide. As is shown later the presumption of reaction occuring between these substances at the temperatures used (809 - 945°K) proved to be correct.

Time did not permit any investigation into the possibility of the reverse reaction between stilbene and hydrogen iodide, or the possibility of the reaction between stilbene and iodine to form a di-iodide. However, it is considered extremely unlikely that hydrogen iodide or iodine would add to stilbene, as the compound formed would be expected to be less stable than

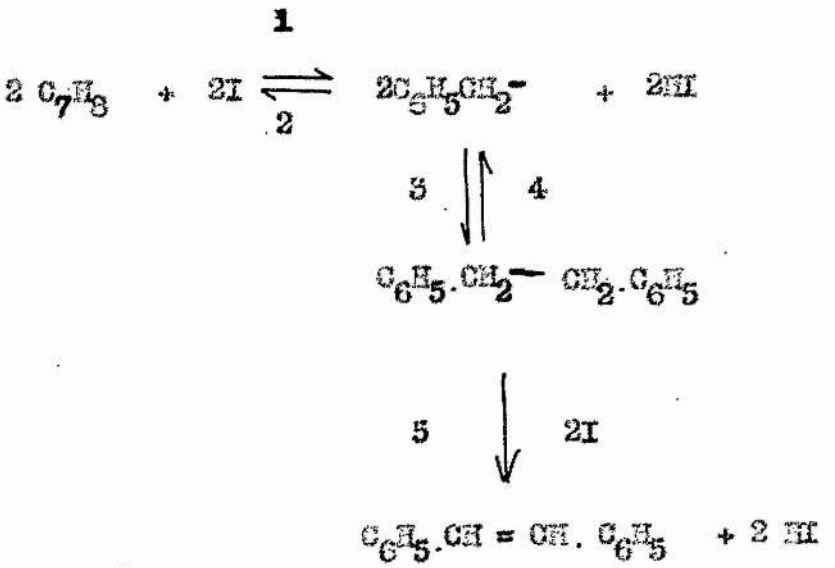

1
2 C_7H_8 + 2I
2
$2C_6H_5CH_2^-$ + 2HI
3
4
$C_6H_5.CH_2 - CH_2.C_6H_5$
5
2I
$C_6H_5.CH = CH.C_6H_5$ + 2 HI

fig (17)

benzyl iodide.

At this stage in the investigation the original reaction between toluene and iodine had proved to be much more complicated than expected, and had branched out into a succession of steps some of which appeared to be reversible.

Secondary processes in the toluene-iodine reaction.

In the reaction scheme laid out in fig.(17) the simplest subject for investigation would appear to be step (5).

Accordingly the reaction of dibenzyl with atomic iodine was studied over the temperature range 809 — 945°K. using dibenzyl concentrations of the same order of magnitude as would have been expected from the quantities of stilbene produced in the toluene-iodine reaction.

A selection of the data obtained is given in Table (16) and shows that

(a) the reaction is very extensive at all temperatures and is distinctly faster than the corresponding reaction between toluene and iodine.

(b) only a small increase in the percentage conversion of dibenzyl to stilbene is observed over the entire temperature range.

(c) the conversion of stilbene is not complete even at 945°K.

This raises the question as to whether there is a simultaneous reaction in which the dibenzyl is converted to some other product.

One possibility is the simultaneous dissociation of dibenzyl (4) to form benzyl radicals followed by reaction with hydrogen iodide to yield toluene and iodine (2).

This reaction between Dibenzyl and Hydrogen iodide was also investigated and the results listed in table (17) show

(d) Over the temperature range 809 to 945°K there is a progressive rise from 4 - 87 % reaction to form iodine. (The contact time held approximately constant 0.26 to 0.31 secs).

(e) The percentage conversion to stilbene shows a parallel rise from 0 to 11%.

(f) In addition experiments 337 - 339 and 340 - 342 show that the percentage conversion to iodine is independent of the hydrogen iodide concentration.

Table 16.

Dibenzyl and Iodine. CT = 0.27 secs. Concentrations moles X 10^{-7}/litre.

P_{N_2} = 3.9 mm. (I) = input concentration of iodine in grm atoms.

No	(DB) IN	(I_2) IN	(HI) EXIT	(St) EXIT	% HI/I	% HI/DB	T°K
287	2.04	9.42	1.72	1.62	9.5	79.6	945
372	3.65	3.67	1.47	2.10	22.0	75.0	898
296	2.63	12.2	0.80	1.06	3.3	40.1	851
293	3.90	12.1	1.95	1.99	8.2	51.0	809

Table 17.

Dibenzyl and Hydrogen iodide. Concentrations moles x 10^{-7}/litre . P_{N_2} = 3.9 mm.

Run No.	DB IN	(I_2) EXIT	(HI) EXIT	(St) EXIT	$\%_{St}/_{DB}$	$\%_{I_2}/_{DB}$	$T^{\circ}K$	C.T. secs.
479	4.69	0.10	6.80	0	0	2.10	809	0.32
480	4.69	0.075	6.80	0	0	1.60	809	0.32
343	4.22	0.225	3.16	0.086	2.04	5.3	832	0.29
344	4.22	0.197	3.99	0.086	2.04	4.7	832	0.29
345	4.22	0.197	4.19	0.086	2.04	4.7	832	0.29
328	2.57	0.315	6.0	0.070	2.56	12.3	851	0.31
329	2.57	0.315	6.78	0.070	2.56	12.3	851	0.31
340	2.73	0.956	6.15	0.302	11.1	35.0	898	0.28
341	2.73	0.956	1.06	0.302	11.1	35.0	898	0.28
342	2.73	1.04	2.08	0.302	11.1	37.9	898	0.28
337	2.09	0.862	0.51	0.233	11.1	41.2	898	0.30
338	2.09	0.862	2.45	0.233	11.1	41.2	898	0.30
339	2.09	0.844	2.94	0.233	11.1	40.4	898	0.30
317	1.88	1.63	0.14	0.17	8.7	87.0	945	0.26
318	1.88	1.42	0.90	0.17	8.7	76.0	945	0.26

Although not listed in the above tables several hydrogen analyses were carried out for both reactions. These showed at $898^{\circ}K$ the ratio of stilbene to hydrogen formed in the reaction of dibenzyl and iodine was 10 : 1. In the reaction between dibenzyl and hydrogen iodide the ratio dropped to 1 : 1.

If we compare the reaction between dibenzyl and iodine with that of toluene and iodine we find that several of the observations listed above (a, b, c,) are in agreement with expectations for two reactions one of which involves the rupture of a primary (C-H) bond and the other the rupture of a secondary (C - H) bond.

The reaction between dibenzyl and iodine would be expected to have a lower activation energy compared with the corresponding reaction between toluene and iodine, since both reactions involve hydrogen abstraction by atomic attack and it is well known that secondary (C - H) bond strengths are weaker than primary bond strengths.

This implies that the $C_{14}H_{13}^{-}$ radical produced in the dibenzyl and iodine reaction instantly forms stilbene so that the initial reaction is the rate determining step. The radical $C_{14}H_{13}^{-}$ will have about the same stability (considering resonance stabilization) as the benzyl radical, however, the analogous back reaction,

$$HI + C_{14}H_{13}^{-} \longrightarrow C_{14}H_{14} + I$$

may be prevented by the possible reaction

$$C_{14}H_{13}^{-} \longrightarrow C_6H_5.CH = CH.C_6H_5 + H \quad .....(6)$$

If this reaction is sufficiently rapid the radical would be destroyed and no back reaction with hydrogen iodide would be possible.

The relatively small change in percentage conversion (b) observed over the entire temperature range could be due to a small energy of activation for the primary step, or at the higher temperature the dibenzyl may have been totally destroyed by two simultaneous reactions. This is in fact suggested by (c, d and e). The hydrogen iodide independence observed in (f) indicates that the dissociation of dibenzyl is the rate determining step followed by a very fast reaction between the benzyl radicals formed and the hydrogen iodide present, e.g.:

$$C_6H_5.CH_2 - CH_2.C_6H_5 \longrightarrow 2\ C_6H_5CH_2 -$$
$$C_6H_5.CH_2 - + HI \longrightarrow C_6H_5.CH_3 + I$$

At 809°K the quantity of stilbene formed as a by-product in the reaction between dibenzyl and hydrogen iodide is small. It was not possible to reduce or eliminate the formation of stilbene by conducting experiments at temperatures lower than 809°K due to the fact that benzyl iodide would be produced at the lower temperatures.

One further point to be considered in the reaction between dibenzyl and iodine is the apparently small variation in the rate of production of stilbene when the iodine concentration is varied threefold at 898°K. (table (18)).

Table 18.

Dibenzyl and Iodine. Concentrations in moles x 10^{-7}/litre.

No.	C.T. secs.	(DB) IN	($2\alpha I_2$) IN	(St) EXIT	(HI) EXIT	T°K
286	0.24	2.04	18.84	1.62	1.73	945
302	0.25	11.34	19.8	7.55	3.00	945
366	0.26	1.19	18.94	1.11	1.25	898
378	0.26	3.21	21.6	2.99	3.60	898
371	0.26	3.64	7.84	2.11	1.47	898
372	0.26	3.64	7.34	2.11	1.46	898
373	0.26	3.64	7.90	2.11	1.58	898
374	0.27	3.65	8.52	2.30	1.47	898
375	0.27	3.65	3.62	2.30	1.59	898

Again it is possible that the dibenzyl may be completely removed at these temperatures due to the simultaneous attack by iodine and the dissociation of dibenzyl itself.

At this stage in these systems of concurrent, consecutive and reversible reactions it became necessary to extend the reaction scheme laid out in fig (17), particularly with reference to the overall step.

$$Ph.CH_2 - CH_2.Ph + 2I \longrightarrow Ph.CH = CH.Ph + 2HI$$

It has already been demonstrated that at those temperatures iodine is almost entirely dissociated and in view of this the initiation step must be,

$$Ph.CH_2 - CH_2.Ph + I \longrightarrow C_{14}H_{13}^{-} + HI \quad \ldots\ldots\ldots(5)$$

followed by the various reaction possibilities available for this $C_{14}H_{13}^{-}$ radical.

$$C_{14}H_{13}^{-} \longrightarrow C_{14}H_{12} + H \quad \ldots\ldots\ldots(6)$$

$$2\,C_{14}H_{13}^{-} \longrightarrow C_{14}H_{12} + C_{14}H_{14} \quad \ldots\ldots\ldots(10)$$

$$C_{14}H_{13}^{-} + C_7H_7^{-} \longrightarrow C_{14}H_{12} + C_7H_8 \quad \ldots\ldots\ldots(11)$$

$$C_{14}H_{13}^{-} + I \longrightarrow C_{14}H_{12} + HI \quad \ldots\ldots\ldots\ldots(12)$$

$$C_{14}H_{13}^{-} + C_{14}H_{13}^{-} \longrightarrow C_{28}H_{26} \quad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

The hydrogen atoms generated in (6) could conceivably react as follows

$$H + I_2 \longrightarrow HI + I \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$H + HI \longrightarrow H_2 + I \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$H + C_{14}H_{14} \longrightarrow H_2 + C_{14}H_{13}^{-} \quad \ldots\ldots\ldots\ldots\ldots (9)$$

$$H + H \longrightarrow H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

Stability of $C_{14}H_{13}^{-}$ radical.

Before considering the above reaction steps it may be convenient to attempt to assess the stability of the dibenzyl radical ($C_{14}H_{13}^{-}$) by thermodynamic calculations.

$$Ph\,CH_3 + I \longrightarrow Ph\,CH_2\text{-} + HI \quad (1)$$

$$Ph\,CH_2\text{-} + HI \longrightarrow Ph\,CH_3 + I \quad (2)$$

$$2\,(Ph\,CH_2\text{-}) \longrightarrow Ph.CH_2.CH_2.Ph \quad (3)$$

$$Ph.CH_2.CH_2.Ph \longrightarrow 2\,(Ph\,CH_2\text{-}) \quad (4)$$

$$Ph.CH_2.CH_2.Ph + I \longrightarrow Ph.\dot{C}H.CH_2.Ph + HI \quad (5)$$

$$Ph.\dot{C}H.CH_2.Ph \longrightarrow Ph.CH = CH.Ph + H \quad (6)$$

$$H + I_2 \longrightarrow HI + I \quad (7)$$

$$H + HI \longrightarrow H_2 + I \quad (8)$$

$$I + I \longrightarrow I_2 \quad (9)$$

$$2\,(Ph\,\dot{C}H\,CH_2\,Ph) \longrightarrow Ph.CH = CH.Ph + Ph.CH_2.CH_2.Ph \quad (10)$$

$$Ph.\dot{C}H.CH_2.Ph + Ph\,CH_2\text{-} \longrightarrow Ph.CH = CH.Ph + Ph\,CH_3 \quad (11)$$

$$Ph.\dot{C}H.CH_2.Ph + I \longrightarrow Ph.CH = CH.Ph + HI \quad (12)$$

$$H + H \longrightarrow H_2 \quad \text{(at wall)} \quad (13)$$

$$2\,(Ph.\dot{C}H.CH_2.Ph) \longrightarrow Ph.CH_2.(Ph).CH\,(Ph).CH.CH_2\,Ph \quad (14)$$

$$Ph.\dot{C}H.CH_2.Ph + HI \longrightarrow Ph.CH_2.CH_2.Ph + I \quad (15)$$

$$Ph\,CH\,CH_2\,Ph + Ph\,CH_2\text{-} \longrightarrow Ph\,CH_2.(Ph)\,CH.CH_2.Ph \quad (16)$$

The calculations given in the appendix (5) show that the process

$$Ph.CH_2 - CH_2.Ph \longrightarrow Ph.CH = CH.Ph + 2H$$

is endothermic to the extent of 127 K cals/mole. This is therefore the energy required for the successive removal of two hydrogen atoms.

The removal of the first hydrogen atom will be expected to involve about 7 K cals less energy than the removal of an alpha hydrogen atom from the toluene molecule. The value of the α(C - H) bond dissociation energy in toluene has been placed between 77.5 and 89.0 K cals/mole which suggests that the endothermicity of the reaction

$$C_{14}H_{14} \longrightarrow C_{14}H_{13}^{-} + H \quad \ldots\ldots\ldots\ldots (6)$$

will lie between 70 and 82 K cals/mole. Consequently the endothermicity for the abstraction of the second hydrogen will lie between 57 and 45 K cals/mole.

If we assume the customary temperature independent factor of 10^{13} and the unimolecular dissociation of the dibenzyl radical occurs in the gas phase we can calculate the half life periods assuming the dissociation requires (1) 57 K cals/mole (2) 45 K cals/mole (table (19))

$$T_{\frac{1}{2}} = \frac{0.69}{k} = \frac{0.69}{10^{13}} \exp\ (-57000/RT) \text{ seconds.}$$

Table (19)

Half life period of ($C_{14}H_{13}^{-}$) radical

$T^{o}K$	Ea	$T_{\frac{1}{2}}$ sec
809	57	174
898	57	5.5
809	45	0.10
898	45	0.018

It is quite obvious therefore that the ($C_{14}H_{13}^{-}$) dibenzyl radical could have a half life period of approximately the same magnitude as the contact time employed in the experiments provided the activation energy for the dissociation lay between 49 and 45 K cals.

If the radical did not decompose inhibition would be feasible due to the back reaction

$$C_{14}H_{13}^{-} + HI \longrightarrow C_{14}H_{14} + I \quad \text{.....(15)}$$

In addition reactions (14) and (16) would also take place forming tetraphenyl butane and triphenyl propane

$$C_{14}H_{13}^{-} + C_{7}H_{7}^{-} \longrightarrow C_{21}H_{20} \quad \text{.....(16)}$$

since these molecules would possess a sufficient number of degrees of freedom to absorb the energy liberated in their formation.

Unfortunately the reaction was already too complicated to allow direct experimental tests for the inhibition predicted by reaction (15) (as will be demonstrated later, benzyl radicals react rapidly with hydrogen iodide over the entire temperature range and would mask step 15) and the mass spectrometer then in use was not capable of handling compounds of such high molecular weight. However it is significant that neither of these compounds was detected in the dibenzyl fraction obtained by chromatographing the solid products formed at 898°K. The evidence would therefore seem to favour the complete and instantaneous dissociation of the dibenzyl radical at that temperature.

However, if the radical was stable especially at the lower temperatures we would have to consider reactions 10, 11, and 12. Processes (10) and (11) are favourable on endothermicity grounds (appendix (6)) but

involving the collision of two radicals they are less likely to take place than process 12. In addition neither reaction (10)nor (11) can account for the ratio of the molecular hydrogen to stilbene produced in the products of the reaction between dibenzyl and hydrogen iodide (1 : 1). Considering the toluene-iodine system at 945°K the minimum ratio of hydrogen iodide to stilbene obtained experimentally was 4 : 1. Assuming reaction (10) takes place and exclusively removes the dibenzyl the minimim ratio would be 6 : 1 and the solid products would consist of a 50/50 mixture of stilbene and dibenzyl. This was not found to be the case.

Considering reaction (11) we have

$$3\ C_7H_8 + 3I \longrightarrow 3\ C_7H_7\text{-} + 3\ HI \quad \ldots\ldots\ldots (1)$$

$$2\ C_7H_7\text{-} \longrightarrow C_{14}H_{14} \quad \ldots\ldots\ldots (3)$$

$$C_{14}H_{14} + I \longrightarrow C_{14}H_{13}\text{-} + HI \quad \ldots\ldots\ldots (5)$$

$$C_{14}H_{13}\text{-} + C_7H_7\text{-} \longrightarrow C_7H_8 + C_{14}H_{12} \quad \ldots\ldots\ldots (11)$$

Overall reaction stoichiometry - $2\ C_7H_8 + 4\ I \longrightarrow C_{14}H_{12} + 4\ HI$.

This satisfies the analytical evidence given above for the toluene-iodine system and in addition the overall stoichiometry of (5) and (11) is

$$C_7H_7\text{-} + C_{14}H_{14} + I \longrightarrow C_7H_8 + C_{14}H_{12} + HI$$

i.e. in the presence of dibenzyl radicals the reaction of dibenzyl with iodine could yield a ratio of 1 mole hydrogen iodide to 1 mole stilbene produced. Therefore, in the range 809 - 945°K where dibenzyl dissociates into benzyl radicals this may be feasible. Inspection of the collected results on the reaction between dibenzyl and iodine does show a ratio of

hydrogen iodide to stilbene formed of approximately 1 : 1. However by using the rate constant for the dissociation of dibenzyl (k_4) derived from the experimental data at 809°K on the reaction between dibenzyl and hydrogen iodide, it is obvious that the rate of dissociation of dibenzyl would be insufficient to sustain the formation of stilbene by this reaction at this temperature.

At 809°K $k_4 = 5.5 \times 10^{-2}$ sec^{-1}. (Runs 477 - 480 Dibenzyl + Hydrogen Iodide).

From Run 293 Dibenzyl + Iodine.

$$\frac{d(St)}{dt} = \frac{1.99 \times 10^{-7}}{.246} = 8.1 \times 10^{-7} \text{ moles litre}^{-1} \text{ sec}^{-1}$$

$$\frac{d(Bz)}{dt} = 2\, k_4\, (DB) = 2 \times 5.5 \times 10^{-2} \times 3.9 \times 10^{-7} = 4.3 \times 10^{-8} \text{ radicals/sec/litre.}$$

Clearly therefore this mechanism would not be able to supply sufficient benzyl radicals at 809°K to enable step (11) to proceed and it too must be ruled out.

There is little objection to reaction (12) in the system dibenzyl plus iodine since the dissociation of the latter is high at the temperatures used. It is clearly less probable in the system dibenzyl plus hydrogen iodide until the iodine produced has built up its concentration to a sufficient degree.

All of the reactions (10), (11) and (12) are in competition with (6) as methods for removing the dibenzyl radical. In the light of the previous calculations indicating a probable short life for it, particularly at the higher temperatures, we must consider the possible hydrogen atom removal reactions (7), (8), (9) and (13).

According to Laidler[92] the activation energy for (7) $H + I_2 \longrightarrow HI + I$ is zero, while for (8) $H + HI \longrightarrow H_2 + I$ the activation energy is 1.5 K cals/mole.

At 898°K therefore if we assume equal temperature independent factors for the two reactions we have equal reaction yields when the concentration of hydrogen iodide is 2.3 times the undissociated iodine concentration, :eg:

$$\frac{d(H_2)}{d(HI)} = \frac{k_1 (HI)(H)}{k_2 (I_2)(H)} \quad \text{or} \quad \frac{k_2}{k_1} = \frac{HI}{I_2} = 2.3.$$

The mean value of the dissociation constant for the iodine concentrationsused at 898°K was of the order of 0.94 and, in view of this, exceptionally small quantities of hydrogen iodide would be sufficient to maintain this system.

Under these conditions, joint operation of these reactions would result in the production of molecular hydrogen without any change in the hydrogen iodide or iodine concentrations.

Reactions (6) together with (9) suggest that a chain mechanism may be possible for the production of stilbene. Such a sequence would lead to the production of large quantities of stilbene and hydrogen catalysed by iodine attack. This is not experimentally observed.

While reaction (13) had to be considered it was clearly of little importance. An atom diffusing to the wall in the presence of an inert gas and the reactant concentrations used would make several hundred collisions of which quite a proportion would be with iodine and hydrogen iodide. The low or zero activation energies involved would ensure

reaction in the homogeneous phase.

There is a further aspect for which the reactions and stability of the dibenzyl radical are important. This is the overall stoichiometry of the reactions.

If we consider the reaction of dibenzyl with iodine the production of one mole of stilbene will be accompanied by two moles of hydrogen iodide or one mole of hydrogen depending on whether the hydrogen atom lost by the dibenzyl radical $C_{14}H_{13}$ attacks an iodine atom or a molecule of hydrogen iodide.

:eg: $C_{14}H_{14} + I \longrightarrow C_{14}H_{13} + HI$ ..... (5)

$C_{14}H_{13} \longrightarrow C_{14}H_{12} + H$ ..... (6)

$H + I_2 \longrightarrow HI + I$ ..... (7)

or $H + HI \longrightarrow H_2 + I$ ..... (8)

If the hydrogen atom is exclusively removed by step (7) then the corresponding ratio of hydrogen iodide to stilbene would be 2/1; on the other hand if the hydrogen atom is removed by step (8) then the ratio is zero. This ratio will therefore have values in the region zero to two depending on the relative participation of steps (8) and (7).

Carrying these considerations back to the toluene and iodine reaction another feature enters into the stoichiometry. The simplest reaction would be

$$2\ C_7H_8 + 2I \longrightarrow C_{14}H_{14} + 2HI$$

which would yield a hydrogen iodide-stilbene ratio of infinity, due to the fact that no stilbene is formed. The opposite extreme would be

complete conversion to stilbene and hydrogen iodide

$$2\ C_7H_8 + 4\ I \longrightarrow C_{14}H_{12} + 4\ HI$$

giving a ratio of four to one.

A ratio of two to one would be obtained if the hydrogen atom dissociated from the dibenzyl radical was exclusively removed by reaction (8).

$$2\ C_7H_8 + 2\ I \longrightarrow C_{14}H_{12} + 2\ HI + H_2.$$

Thus, starting from toluene and iodine one can visualise ratios of hydrogen iodide to stilbene produced in the range from two to one to infinity. A discussion of the stoichiometries actually found will be given later.

Thermodynamic Estimation of Equilibrium Possibilities in the Reaction System.

The reaction scheme put forward contains two sets of reversible reactions

A $\quad C_7H_8 + I \longrightarrow C_7H_7 + HI. \qquad (1)\ \&\ (2).$

B $\quad C_{14}H_{14} \longrightarrow 2\ C_7H_7. \qquad (3)\ \&\ (4).$

Before proceeding to turn the qualitative examination of the data given above into a more quantitative form it may be helpful to consider the possible proportions of reactants and products in these systems if equilibrium was attained. In order to do this it is necessary to calculate approximate values of ΔG° for the reactions.

Equilibrium A

Let ΔH° be the change in heat content at unit pressure

$$\Delta H^{\circ} = D(PhCH_2 - H) - D(H - I)$$
$$= D(PhCH_2 - H) - 71$$

If we assume the limiting values for $D(PhCH_2 - H) = 78$ and 89.5 K cals/mole the corresponding values of ΔH° would be 7 and 18.5 K cals/mole respectively

Now $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$.

The entropy change for the reaction involves an estimation of the entropy of the benzyl radical. This is likely to be very similar to the entropy of toluene at the same temperature if an allowance is made for the electron entropy due to the unpaired electron. According to Trotman - Dickenson[40] this may be adequately accounted for by an increment of 1.4 e.u. At 298°K the standard entropies are,

$(HI)_g$ - Hydrogen iodide 49.31 eu.

$(I)_g$ - Iodine 43.18 eu.

Thus the total ΔS° term could be 7.53 eu at 298°K.

To obtain the value of ΔS at 898°K, we require values of the specific heats of iodine and hydrogen iodide at constant pressure.

C_p° iodine = 4.97 cals/degree C_p° hydrogen iodide = 6.97 cals/degree

Hence:- $\Delta C_p^{\circ} = 12$ cal/degree.

and assuming ΔC_p° is independent of temperature we have

At 898°K = T

$$\Delta S_T = 7.53 + \Delta C_p^{\circ} \int_{T_1}^{T_2} d \operatorname{Log}_e T$$
$$= 7.53 + \Delta C_p^{\circ} \operatorname{Log}_e \frac{T_2}{T_1}$$
$$= 7.53 + 4.6 \operatorname{Log}_{10} 3 = 9.73 \text{ eu.}$$

$\therefore$ at 898°K

$$\Delta G^{\circ} = 7000 - (898 \times 9.73) = -1.750 \text{ K cals.}$$

or $$\Delta G^{\circ} = 18500 - (898 \times 9.73) = +7.77 \text{ K cals.}$$

and $$\Delta G^{\circ} = -RT \log_e Kp$$

$$Kp = 10^{-\Delta G^{\circ}/4.57\,T}$$

Hence at 898°K if ΔH° = 7 K cals/mole $Kp = 10^{.42}$, $Kc = 2.63$

if ΔH° = 18.5 K cals/mole $Kp = 10^{-1.9}$, $Kc = 1.26 \times 10^{-2}$.

At 898°K therefore the equilibrium mixture will contain excess toluene and iodine only if the toluene bond dissociation energy is approximately 89 K cals.

At 809°K $\Delta G^{\circ} = -700$ cals

or $\Delta G^{\circ} = 10.8$ K cals

and we get the corresponding values $K_c = 1.55$ or 1.26×10^{-3}.

The equilibrium mixture would be expected to contain an excess of toluene and iodine for temperatures in the region of 809 - 898°K only if the value of the α(C - H) bond dissociation energy for toluene is in the region of 89 K cals. Using Szwarc's value of 77.5 K cals/mole the equilibrium mixture would contain an excess of benzyl radicals and hydrogen iodide.

Equilibrium B

$$C_{14}H_{14} \longrightarrow 2\ C_7H_7\text{-}$$

This is rather more difficult to estimate, for the entropy of dibenzyl is not known; however, we may derive an approximate value from the empirical observation that for compounds in the gas phase it would appear that

$$S^{\circ}(XY) = \frac{S^{\circ}(X_2) + S^{\circ}(Y_2)}{2}$$

(all data from Handbook Chem and Phys 1753, 37, 1956).

e.g.

Ethane $(CH_3)_2$ S° = 54.85 eu.

CH_4 S° = 44.5 eu. $S^\circ(CH_4)$calc = $\frac{54.85 + 31.21}{2} = 86/2 = 43$ eu.

H_2 S° = 31.21 eu.

and octane $(C_4H_9)_2$ S° = 110eu. Check (H_2) S° = 31.21 eu.

(PhC_4H_9) S° = 104 eu. (PhH) S° = 64 eu.

Hence (Ph - Ph) calc S° = 98 eu. $\therefore$ (Ph - Ph) S° = 97 eu.

We may apply this system to the following data.

(H_2) S° = 31.21 eu. $(PhCH_2 - H)$ S° = 76.42 eu. $\therefore S^\circ(PhCH_2CH_2Ph)$ = 121.63 eu.

and

$(PhCH_2 - Me)$ S° = 86.15 eu $(Me)_2$ - S° = 54.85 eu. $\therefore S^\circ$ $(PhCH_2CH_2Ph)$ = 117.2 eu.

The approximate standard entropy of dibenzyl is 120 eu.

As in the previous case we may assume $S^\circ(C_7H_7-)$ = $S^\circ(C_7H_8)$ + 1.4 eu

= 76.42 + 1.4 = 77.82

$C_{14}H_{14} \longrightarrow 2\ C_7H_7$ ΔS° = 35.64 eu.

At 25°C $Cp(C_{14}H_{14})$ = 66.1 $Cp(C_7H_8) \fallingdotseq Cp(C_7H_7-)$ = 37.05

$\Delta Cp \fallingdotseq 8$ $\Delta S_{T_1}^{T_2} = \Delta Cp \log_{10} \frac{T_2}{T_1}$ = 4 eu

ΔS°_{898} = 39.64 eu. $T\Delta S^\circ$ = 35,600 cals.

If ΔH° = 48 K.cals. $\Delta H^\circ - T\Delta S^\circ$ = 12.4 K. cals = ΔG°

$K_p = 10^{-\Delta G^\circ/RT}$ $K_c = K_p/RT$

$K_c = 10^{-7.43}$

Consequently with the smallest value possible for $D(C_7H_7 - C_7H_7)$ benzyl radicals should dimerise almost completely at all temperatures experimentally selected.

The Reaction Dibenzyl and Hydrogen iodide.

The data for experiments 479 and 480 at 809°K (table 17) show that stilbene production was negligible and as a result a first order rate constant for the dissociation of dibenzyl may be calculated at this temperature without any treatment for secondary reactions. The value obtained at 809°K. $k_4 = 5.8 \times 10^{-2}$ sec $^{-1}$, together with an assumed frequency factor of 10^{13} suggests an energy of activation in the region of 53 K cals/mole for the dissociation process.

At higher temperatures table 17 shows clearly the need to deal with the two processes which are responsible for the removal of dibenzyl. The data obtained in the region 851 - 898°K show that considerable quantities of stilbene are formed.

Previous discussion in the qualitative section showed that the following reaction scheme would be suitable for the reaction between dibenzyl and iodine

$$C_{14}H_{14} + I \longrightarrow C_{14}H_{13}^{-} + HI \qquad (5)$$

$$C_{14}H_{13}^{-} \longrightarrow C_{14}H_{12} + H \qquad (6)$$

$$H + HI \longrightarrow H_2 + I \qquad (7)$$

$$H + I_2 \longrightarrow HI + I \qquad (8)$$

and it was concluded that the quantity of hydrogen produced per molecule of stilbene could vary with the quantities of hydrogen iodide and iodine in the system.

Returning to the experimental data it is found that mass spectrometric analysis of the products obtained in the reaction between dibenzyl and hydrogen iodide showed stilbene and hydrogen were produced in equimolecular amounts at all temperatures. Table (20) shows that in most cases the quantity of stilbene formed was quite small in comparison to the iodine generated.

Table 20.

Dibenzyl and Hydrogen iodide. $P(N_2)$ 3.9mm.

All concentrations moles x 10^{-7}/litre.

Run No.	(DB) IN	(HI) IN	(I_2) EXIT	(St) EXIT	(H_2) EXIT	T°K	C.T. sec.
317	1.88	3.40	1.63	0.165	0.22	945	0.26
319	2.28	5.50	0.14	0	0.007	809	0.31
322	1.97	4.78	0.94	0.23	0.22	898	0.26
325	1.9	4.15	1.57	0.20	0.21	945	0.27

The presence of toluene amongst the reaction products was confirmed. Variation of the input hydrogen iodide concentration had no effect on the rate of production of iodine, and due to the experimental technique employed, the effect on the hydrogen and stilbene production was not estimated in each individual run. (See experimental section).

In view of the qualitative experimental evidence the following overall reaction scheme is postulated :-

$$(C_7H_7 - C_7H_7) \longrightarrow 2\ C_7H_7^- \qquad (4)$$

$$C_7H_7^- + HI \longrightarrow C_7H_8 + I \qquad (2)$$

$$I + (C_7H_7 - C_7H_7) \rightarrow C_{14}H_{13}^- + HI \qquad (5)$$

$$C_{14}H_{13}^- \longrightarrow C_{14}H_{12} + H \qquad (6)$$

$$H + I_2 \longrightarrow HI + I \qquad (7)$$

$$H + HI \longrightarrow H_2 + I \qquad (8)$$

To simplify the analytical discussion we will take the two extreme cases a. in which the hydrogen atom found in (6) is exclusively removed by step (8) resulting in a molecule of hydrogen per molecule of stilbene produced. b. in which the hydrogen atom formed in (6) is removed by (7) thus yielding two molecules of hydrogen iodide per molecule of stilbene produced.

a. Catalytic production of stilbene with no iodine consumption.

$$C_7H_7 - C_7H_7 \longrightarrow 2\ C_7H_7^- \qquad (4)$$

$$C_7H_7^- + HI \longrightarrow C_7H_8 + I \qquad (2)$$

$$C_{14}H_{14} + I \longrightarrow C_{14}H_{13}^- + HI \qquad (5)$$

$$C_{14}H_{13}^- \longrightarrow C_{14}H_{12} + H \qquad (6)$$

$$H + HI \longrightarrow H_2 + I \qquad (8)$$

At any time t, let y = concentration of iodine, and z the concentration of stilbene.

Then

$$dy/dt = k_4 (C_{14} H_{14})$$

$$dz/dt = k_5 (C_{14} H_{14})(2aI_2)$$

$$dy/dz = \frac{1}{2By} \qquad \ldots\ldots (17) \text{ where } B = \frac{k_5 a}{k_4}$$

Integrating $z + c = By^2$ at $t = o$ $z = o$ $y = o$.

$\therefore c = o$

$$z = By^2 \qquad \ldots\ldots (17a)$$

Now

$$dy/dt = k_4 (C_{14} H_{14})$$

$$k_4\, dt = dy/(C_{14} H_{14}) = dy/(a-y-z) = dy/(a-y-By^2)$$

Completing the square

$$- y - By^2 = \frac{1}{4B} - \frac{1}{4B}(2By + 1)^2$$

$$\int_o^t k_4\, dt = 2 \int_{\theta=1}^{\theta=\theta} d\theta/(d^2 - \theta^2)$$

where $\theta = 2By + 1$ $\quad d\theta = 2Bdy$ $\quad d^2 = 4aB+1$.

Integrating we have

$$k_4 = \frac{2.3}{td} \operatorname{Log}_{10} \frac{(\theta + d)(1 - d)}{(\theta - d)(1 + d)} \qquad \ldots\ldots (18)$$

Case b. $C_{14}H_{14} \longrightarrow 2\,C_7H_7 -$ (4)

$C_7H_7 - + HI \longrightarrow C_7H_8 + I$ (2)

$C_{14}H_{14} + I \longrightarrow C_{14}H_{13} + HI$ (5)

$C_{14}H_{13} \longrightarrow C_{14}H_{12} + H$ (6)

$H + I_2 \longrightarrow HI + I$ (7)

$$dy/dt = k_4 (C_{14}H_{14}) - k_5 (C_{14}H_{14})(2\alpha I_2).$$

$$dz/dt = k_5 (C_{14}H_{14})(2\alpha I_2).$$

$$dy/dz = \frac{1}{2By} - 1. \qquad (19)$$

Integrating $$z = \frac{1}{2B} \log_e \left(\frac{1}{1-2By}\right) - y.$$

or

$$y + z = \frac{2.3}{2B} \log_{10} \left(\frac{1}{1-2By}\right) \qquad (20)$$

Now $$dy/dt = k_4(C_{14}H_{14}) - k_5 (C_{14}H_{14})(2\alpha I_2)$$

$$= k_4 (C_{14}H_{14}) (1 - 2By)$$

$$\therefore k_4 dt = dy \Big/ \left\{(a - (y + 2z)\right\} (1 - 2By)$$

At time t dibenzyl lost = iodine formed + stilbene + iodine removed to form stilbene = $(y + 2z)$.

Hence $$k_4 dt = dy \Big/ \left\{(a + y - \frac{1}{B} \log_e \left(\frac{1}{1-2By}\right)\right\} (1 - 2By)$$

By expanding the log term we have

$$y - \frac{1}{B} \operatorname{Log}_e \left(\frac{1}{(1-2By)} \right) = - y - 2By^2 - (8/3)B^2y^3.$$

As will be shown later the practical values of B and y mean that the last term is not negligible.

To integrate it is necessary to complete the cube which gives the nearest approximation.

$$\frac{1}{6B} - \frac{1}{6B} \left\{1 + 2By\right\}^3 = - y - 2By^2 - (8/6)B^2y^3.$$

As will be shown later this form is valid to within 10% for all values of y formed at 898°K

if $\theta = (2By + 1)$ and $d^3 = 6aB + 1$ $\quad d\theta = 2Bdy$

$$\int k_4 dt = 3 \int d\theta / (d^3 - \theta^3)(2 - \theta)$$

$$= 3 \int d\theta / (d^3 - \theta^3)(\theta)(2/\theta - 1).$$

Splitting it into partial fractions and integrating we have

$$k_4 = \frac{1}{t} \left[\frac{2.3d}{(2-d)(d)^3} \operatorname{Log}_{10} \frac{\theta^3 (d^3-1)}{(d^3 - \theta^3)} + \frac{3}{(d^3-8)} \left\{1-\theta-4.6 \operatorname{Log}_{10} (2 - \theta)\right\} \right] \quad (21)$$

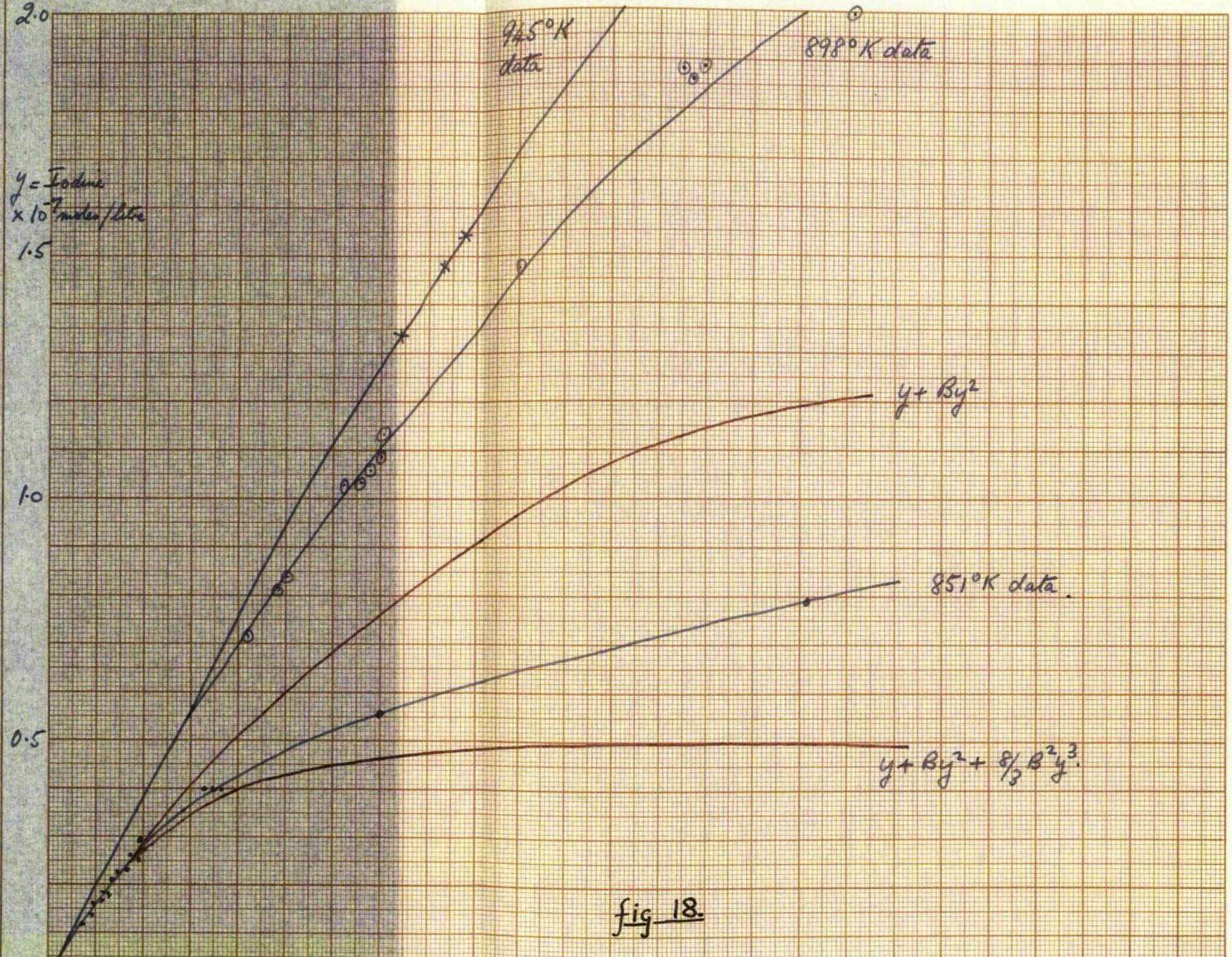

2.0
1.5
1.0
0.5
y = Iodine
× 10⁻⁷ moles/liter
945°K
data
898°K data
y + By²
851°K data.
y + By² + 8/3 B² y³.

fig 18.

Application of the expressions 17a and 20.

The sum of the iodine and stilbene concentrations formed can be readily obtained from experimental data. Expression (17a) may be modified to the form

$$y + z = y + By^2. \qquad (17b).$$

Likewise expression (20) may be expanded

$$y + z = \frac{1}{2B} \text{Log}_e \frac{1}{1-2By} = y + By^2 + (4/3)B^2y^3. \qquad (20a)$$

Thus (17b) and (20a) both relate the iodine concentration to the sum of the iodine and stilbene concentrations by means of the constant B. At small values of B and y, $(4/3)B^2y^3$ will be negligible and both expressions will yield the same initial plot.

In order to see whether these expressions bore any relationship to the experimental data the following graphical method of solution was evolved. A series of curves were plotted for y against $y + z = \frac{1}{2B} \text{Log}_e \frac{1}{1-2By}$ using arbitrarily chosen values for B. The experimentally found values for y and (y + z) were then inserted on the graph for each temperature and the appropriate values of B selected by inspection from the family of curves. These values of B were then used in the above equation to calculate the values of $\frac{1}{2B} \text{Log}_e \frac{1}{(1-2By)}$ and $y + By^2$ for known values of y and the corresponding curves plotted to check the fit with the experimental data.

As can be seen in fig.(18) only at 851°K was sufficient experimental data available to compare the fit with both formulae (17b and 20). These plots clearly show that initially the reaction

produces stilbene catalytically, but at the higher concentrations and longer contact times which yield higher quantities of iodine in the products, there is an increasing consumption of iodine although this is not as large as predicted by (20a). This is due to the point mentioned previously that once the hydrogen iodide-iodine ratio has reached a certain value in the system, the simultaneous operation of both (7) and (8) will produce molecular hydrogen without affecting the concentrations of hydrogen iodide or iodine present.

Any attempt to derive an expression to fit the experimental curve at 851°K of $(y)v(y+z)$ would therefore require a knowledge of the instantaneous relative concentrations of hydrogen iodide and iodine in the system and their function with time, e.g.

$$H + I_2 \longrightarrow HI + I \qquad (7)$$

$$H + HI \longrightarrow H_2 + HI \qquad (8)$$

Let p molecules of hydrogen and q moles of hydrogen iodide be formed by steps (8) and (7) respectively together with (p + q) moles of stilbene.

Then $dy/dt = k_4 (C_{14}H_{14}) - \frac{q}{p+q} (C_{14}H_{14})(2\alpha I_2)$.

as before $dz/dt = k_5 (C_{14}H_{14})(2\alpha I_2)$.

$$dy/dz = \frac{1}{2By} - \frac{q}{(p+q)}$$

$$= \frac{1}{2By} - \frac{(1-\alpha)\, k_7(I_2)}{(1-\alpha)k_7(I_2) + k_8(HI)}. \qquad (22)$$

This equation contained too many variables for integration, for not only are the functions for the variations of hydrogen iodide and iodine concentrations with time required, but also the variation of the

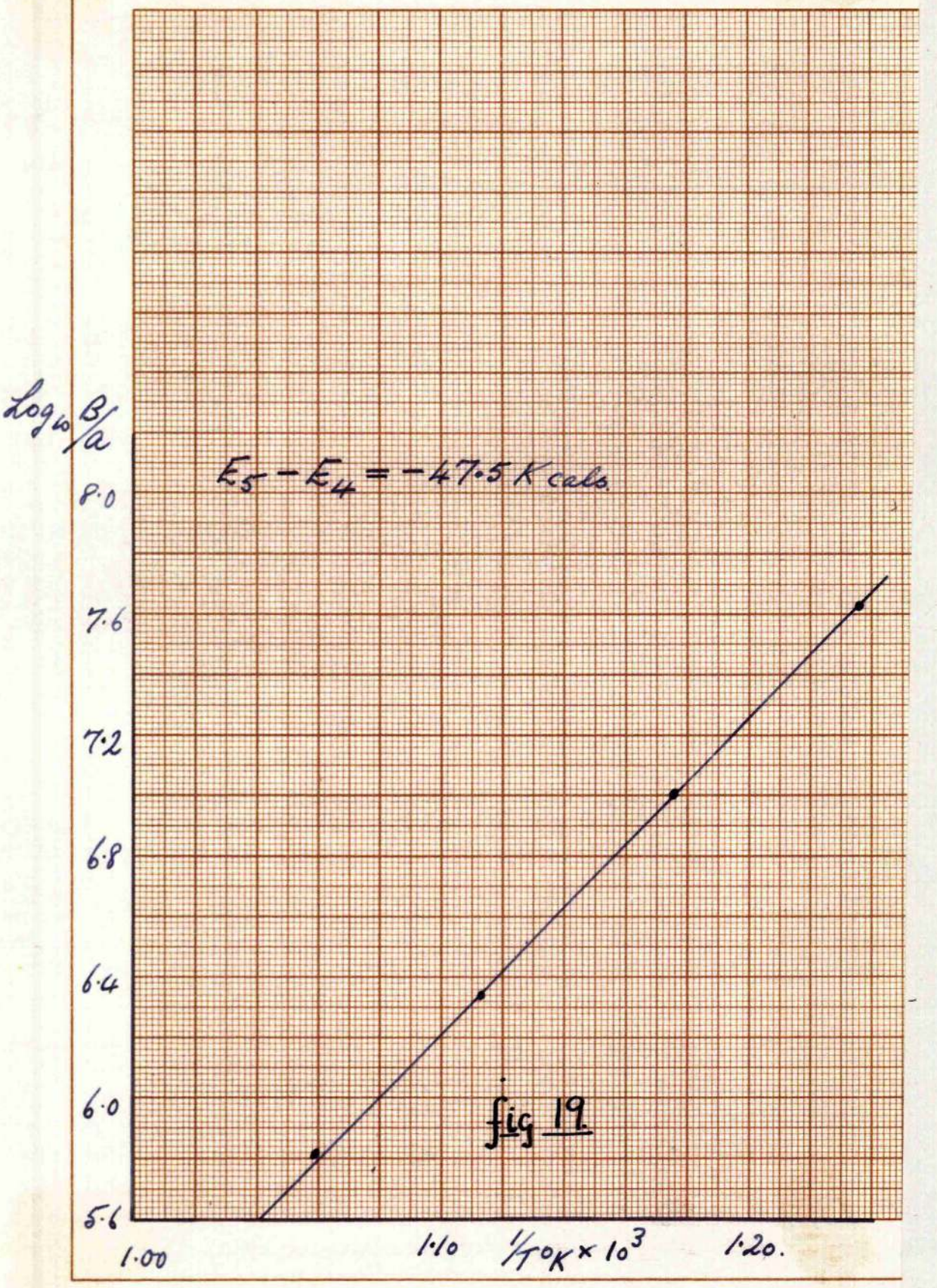

$\log_{10} B/a$
$E_5 - E_4 = -47.5$ K cals.
8.0
7.6
7.2
6.8
6.4
6.0
5.6
1.00
1.10
$1/T°K \times 10^3$
1.20.

fig 19

dissociation constant a with the varying iodine concentration.

This attempt to find an expression to fit the experimental curve was therefore abandoned and instead the values of B were obtained from the experimental points (where $(y + z) \approx y$) which satisfied both equations (17b) and (20a).

Derivation of $(E_5 - E_4)$.

The graphically obtained values of B are shown in table (21) together with the ratio B/a = k5/k4 at 809°K the ratio k5/k4 was worked out directly from the values of k4 and k5, for at this temperature and at the concentrations employed both reactions are virtually independent of one another. (See Runs 292 - 294 and 476 - 481).

At 809°K $k_4 = 0.056$ $k_5 = 0.23 \times 10^7$

$B/\alpha = k_5/k_4 = 44.1 \times 10^6$.

Table (21).

Evaluation of B.

T°K	$10^3/T°K$	$B \times 10^{-6}$	α	$\frac{B}{\alpha} \times 10^{-6}$	Log B/α
945	1.059	0.6	1.0	0.60	5.806
898	1.114	2.2	0.98	2.25	6.350
851	1.175	10.0	0.94	10.65	7.030
809	1.236	44.1	-	41.0	7.613

Fig. (19) shows a plot of $(\log_{10} B/\alpha) v (1/T)$. With the exception of the point at 945°K a linear relationship is obtained. The slope of this line yields an energy of activation difference of - 47.5 K cals. By definition $B = k_5\alpha/k_4$.

$\therefore \log_{10} B/\alpha = \log_{10} k_5/k_4 = \log_{10} A_5/A_4 - (E_5 - E_4)/ 2.3RT$ ....(22)

$\therefore E_5 - E_4 = -47.5$ K cals/mole.

$E_4 = 47.5 + E_5$ K cals/mole.

Determination of E.5.

We may use expression (22) to determine E_5. It will be assumed that A_4 is approximately 10^{13} a value which is to be expected on theoretical grounds for any first order dissociation. At 809°K

$$\frac{1}{T} = 1.236 \times 10^{-3} \quad \text{Log}_{10} B/\alpha = 7.68 \qquad \left(\Delta E/4.57_T\right) = -12.88$$

$\therefore$ $\text{Log}_{10} A_5/A_4 = -5.2.$

Assume $A_4 = 10^{13}$ $\quad \text{Log}_{10} A_4 = 13.$

$\therefore$ $\text{Log}_{10} A_5 = 7.8$

$A_5 = 10^{7.8} = 4.8 \times 10^7$

Taking the results of experiments 292 - 294 on the system dibenzyl and iodine we find at 809°K

$$k_5 = 2.3 \times 10^6 = 10^{6.36}$$
$$= 10^{7.8} \times 10^{-E/3700}$$

$\therefore$ $E_5 = 5.34$ K cals/mole.

$\therefore$ $E_4 = 47.5 + 5.34$

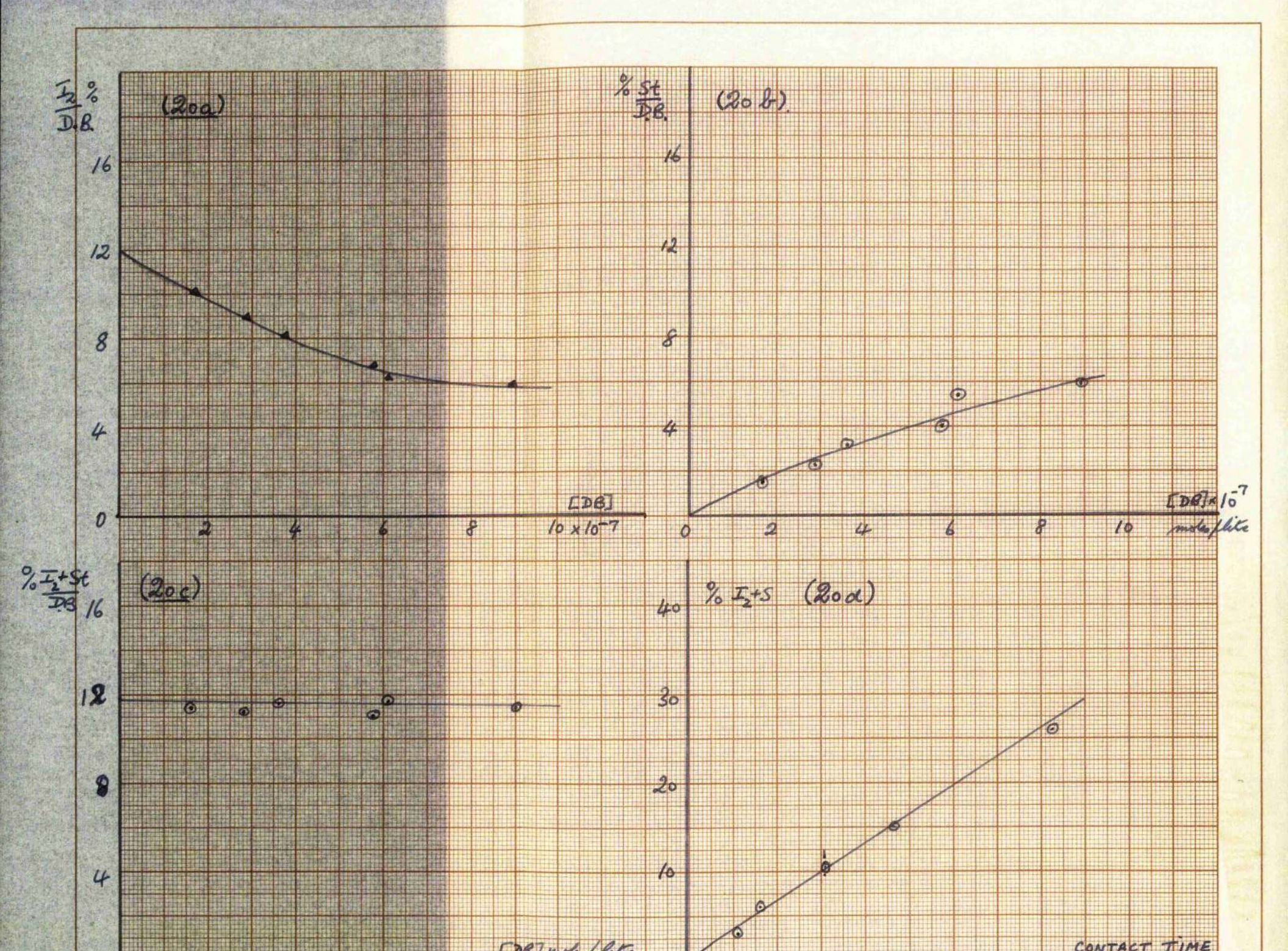
$= 52.84$ K cals/mole.

Direct determination of k_4.

The direct determination of k_4 requires an expression which will allow for other depletion of dibenzyl due to the simultaneous secondary reaction forming stilbene. At the lower temperatures between 809°K and 840°K little stilbene is formed and k_4 may be calculated by the conventional first order equation.

$$k_4 = \frac{2.3}{t} \text{Log}_{10} \frac{a}{(a - x)}$$

where a = original dibenzyl and (a - x) the dibenzyl concentration at time t. At 851°K and 898°K sufficient data was available to allow graphical methods to be used.


(20a)
% I2 / D.B.
16
12
8
4
0
2
4
6
8
[DB] 10 x 10⁻⁷
(20 b).
% St / D.B.
16
12
8
4
0
2
4
6
8
10
[DB] x 10⁻⁷ mole/litre
(20c)
% I2+St / DB
16
12
8
4
% I2+S (20d)
40
30
20
10
CONTACT TIME

The data at 851°K will be dealt with first.

Four graphs are shown in fig.(20). Fig.(20a) shows the percentage conversion to iodine falls off as the dibenzyl concentration is increased, whereas fig.(20b) shows that the percentage conversion to stilbene is nearly linear with dibenzyl concentration for the small percentages involved. It would be expected that a plot of the percentage dibenzyl converted to iodine and the percentage converted to iodine and stilbene would intersect at infinitely small dibenzyl concentration if both reactions proceeded simultaneously and started at the same time. Due to the speed of the separate reactions and the relatively long contact time employed (0.31 sec.) they may be considered to have started simultaneously, and the intersection of the two curves would yield a value for the maximum percentage dissociation in terms of iodine found. (At this point the stilbene would be zero and even if it were argued that stilbene was present at this point of intersection, then the high hydrogen iodide concentration would ensure that it was formed catalytically). Fig.(20c) shows that these curves do intersect at approximately zero input dibenzyl concentration to yield a value of 11.9% decomposition, giving $k_4 = 0.375$ sec.$^{-1}$.

One peculiar feature of fig.(20c) is that the percentage conversion to stilbene and iodine is almost independent of the input dibenzyl concentration and demonstrates a "pseudo" first order characteristic. Fig.(20d) in which the total percentage conversion to stilbene and iodine is plotted against contact time, demonstrates a

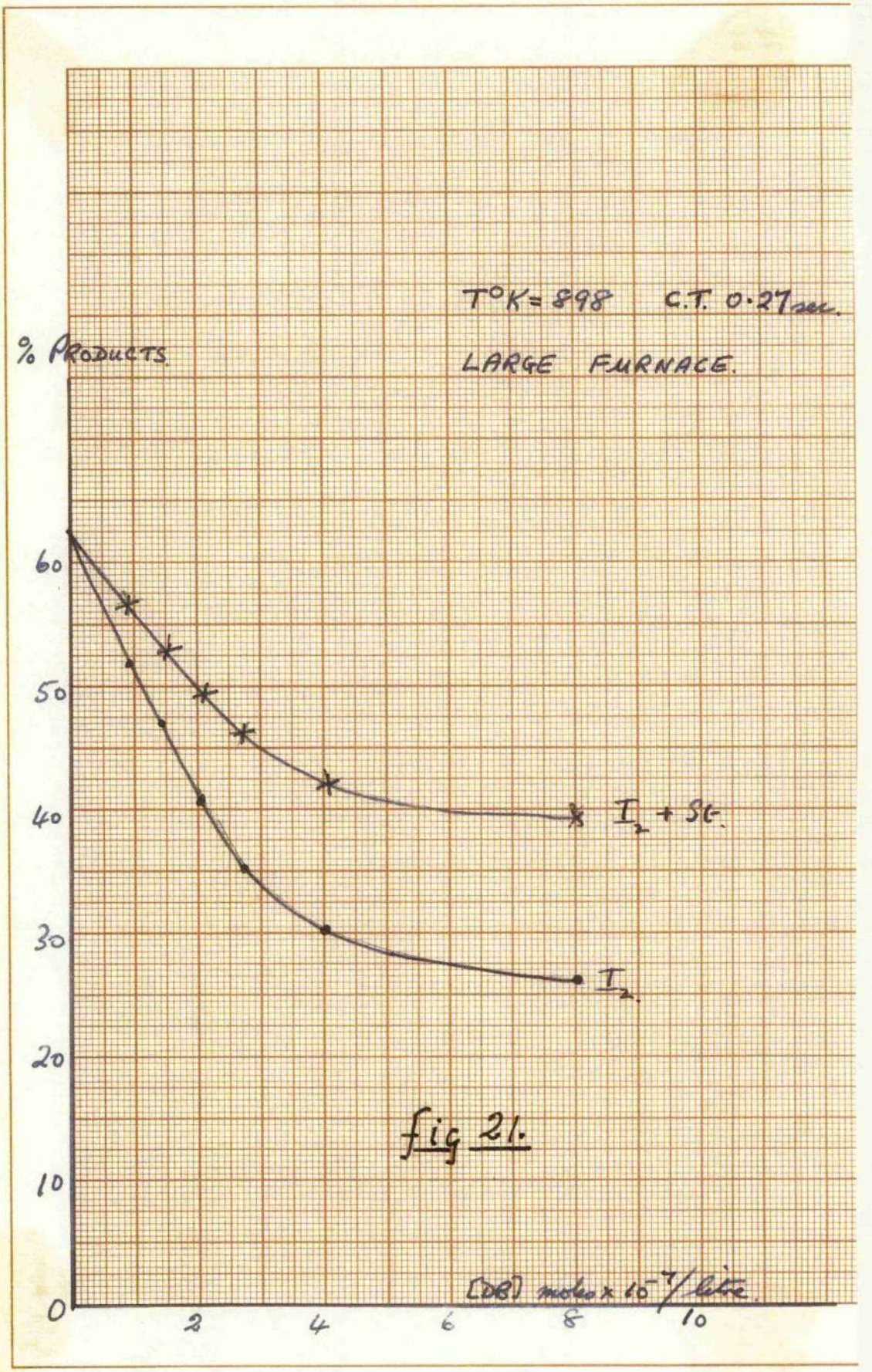

T°K = 898 C.T. 0·27 sec.
LARGE FURNACE.
% PRODUCTS
60
50
40
30
20
10
0
2
4
6
8
10
I₂ + St.
I₂
[DB] moles × 10⁻⁷/litre.

fig 21.

better than normal characteristic for a first order reaction since the percentage conversion would not be expected to show a linear relationship with time but at the high percentage conversions achieved would be expected to fall off slightly.

This effect may be purely fortuitous for a similar extrapolation of data at 832°K showed that extrapolation produced a smaller k_4 value, whereas extrapolation at 874 and 898°K produced a higher k_4 value. It is therefore seen that below 851°K, values of $k_4 = \frac{2.3}{t} \text{Log} \frac{a}{(a-y-z)}$ have been overcorrected for the quantity of iodine lost in the formation of stilbene.

Fig.(21) shows a similar plot for data obtained at 898°K. Again the two curves intersect at infinitely dilute dibenzyl concentrations and indicate a percentage conversion of 62.5%, yielding a k_4 max. of 3.65 sec.$^{-1}$.

These two extrapolated values of k_4 at 851°K and 898°K together with k_4 values derived at lower temperatures were used to determine E_4 directly by the Arrhenius plot (fig.(22)). A linear relationship was obtained between $\text{Log}_{10} k_4$ and $1/T°K$ over the entire range of temperatures employed, leading to a value of 61.0 K cals/mole for the dissociation energy of dibenzyl and a temperature independent factor $A = 10^{15.4}$.

$$\frac{E_4}{A_4} = \frac{61.0 \text{ K cals/mole}}{10^{15.4}}$$

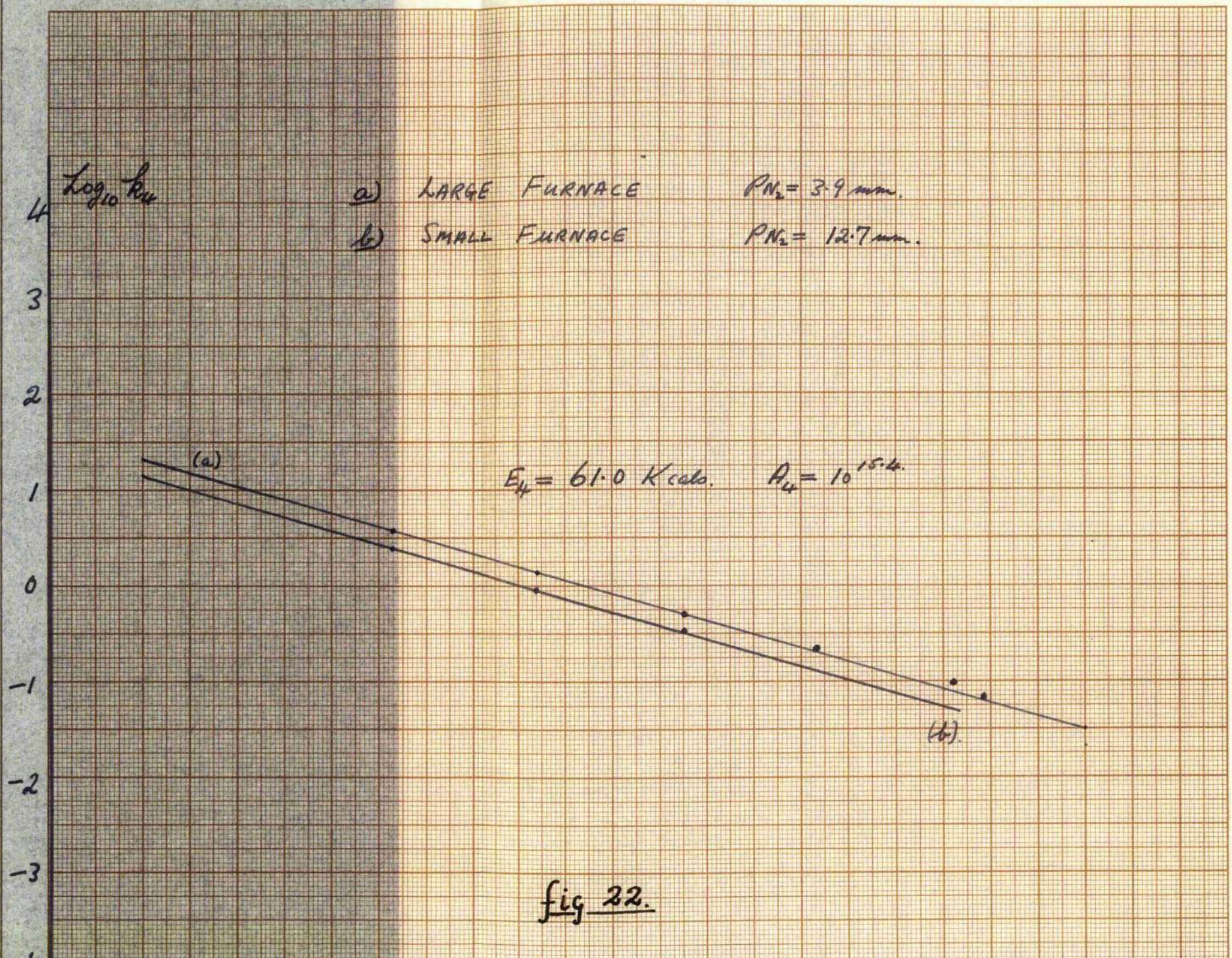

$\log_{10} k_4$
a) LARGE FURNACE $P_{N_2} = 3.9$ mm.
b) SMALL FURNACE $P_{N_2} = 12.7$ mm.
4
3
2
1
0
−1
−2
−3
(a)
(b)
$E_4 = 61.0$ K cals. $A_4 = 10^{15.4}$.

fig 22.

This value for E_4 is not in good agreement with the indirectly calculated value of 53 K cals obtained from the Arrhenius plot of $Log_{10} B/a$ v $^1/_T{}^oK$ and employing an assumed temperature independent factor $A_4 = 10^{13}$.

However, it is interesting to note that if $A_4 = 10^{15.4}$ is substituted in the previous calculations in place of $A_4 = 10^{13}$, the calculated value of E_5 would rise from 5.34 to 14.05 K cals/mole, giving a value of 61.55 K cals for E_4 in complete agreement with the above value obtained directly by the Arrhenius plot of $Log_{10} k_4$.

Derivation of an expression for rate constant k_4.

Before proceeding further it will be convenient to examine the possibilities of obtaining an expression for k_4 which would hold under all experimental conditions. It has already been pointed out that in the secondary reaction, the production of stilbene, the products produced are profoundly affected by the ratio of hydrogen iodide to iodine, and that molecular hydrogen would be produced without altering the ratio. Since hydrogen iodide is in excess initially, molecular hydrogen will be produced almost exclusively until the iodine concentration builds up. Above a certain value of the iodine concentration iodine will be converted into hydrogen iodide to replace the hydrogen iodide consumed by the primary process and thus preserve the critical ratio, e.g.

$$2\,C_7H_7- + 2HI \longrightarrow 2\,C_7H_8 + 2I$$

$$2I + 2\,C_{14}H_{14} \longrightarrow 2\,C_{14}H_{13}- + 2HI$$

$$2\,C_{14}H_{13}- \longrightarrow 2\,C_{14}H_{12} + 2H$$

$$H + HI \longrightarrow H_2 + I$$

$$H + I_2 \longrightarrow HI + I$$

$$I + I \longrightarrow I_2$$

It is therefore apparent that molecular hydrogen will be produced in equivalent amounts to the stilbene initially but will fall off to half this value as the critical ratio of hydrogen iodide to iodine is approached. In view of this, equation (21) which was based on the complete formation of two molecules of hydrogen iodide per molecule of stilbene produced, will be completely invalid under all experimental conditions and need not be considered further.

As previously remarked, equation (22) which takes into consideration the variation of the hydrogen iodide - iodine ratio contains too many unknowns and cannot be solved.

Equation (18) based on the catalytic production of stilbene without the loss of iodine is only suitable at very small dibenzyl concentrations and small contact times where the simple formula

$$k_4 = \frac{2.3}{t} \quad \mathrm{Log}_{10}\frac{a}{(a-x)}$$

is equally applicable since the stilbene concentrations are quite small. Table (22) shows that both the simple first order expression and the complex expression (18) fail to yield a constant k_4 when iodine is consumed. This is to be expected for neither allow for the iodine

depletion and in addition the simple expression does not allow for the depletion of dibenzyl due to stilbene production.

At 851°K the empirical expression $k_4 = \frac{2.3}{t} \text{Log}_{10}\left(\frac{a}{(a-y+z)}\right)$ ...(23) yields consistent values of k_4 for all the data at that temperature.

At 898°K for very small contact times (0.18 sec.) and small input dibenzyl concentrations the empirical expression yields values quite near to the extrapolated value obtained from fig.(21), but is hopelessly inadequate for moderate concentrations of dibenzyl and longer contact times. (table (22)).

Table (22).
Estimation of k_4.

Dibenzyl and Hydrogen iodide. Contact time variation.

All concentrations moles x 10^{-7}/litre.

Column A $k_4 = \frac{2.3}{t} \text{Log}_{10} {}^{a}/_{(a-\overline{y+z})}$ .....(22)

PN_2 = 3.9 mm. Column B $k_4 = \frac{2.3}{t} \text{Log}_{10} {}^{a}/_{(a-y)}$ .....(23)

Column C $k_4 = \frac{2.3}{td} \text{Log}_{10} \frac{(\theta+d)(1-d)}{(\theta-d)(1+d)}$ .....(18)

Run No.	C.T. secs.	(DB) IN	(I_2) EXIT	(St) EXIT	A	B	C	T^oK
441	0.112	7.86	0.217	0.023	0.268	0.253	0.245	851
442	0.112	7.86	0.215	0.023	0.238	0.233	0.245	851
443	0.160	4.60	0.226	0.036	0.367	0.305	0.32	851
444	0.160	4.60	0.236	0.036	0.367	0.305	0.32	851
445	0.160	4.60	0.226	0.036	0.367	0.305	0.32	851
455	0.31	8.93	0.490	0.53	0.408	0.187	0.181	851
456	0.31	8.93	0.497	0.53	0.408	0.187	0.181	851
457	0.31	8.93	0.497	0.53	0.408	0.187	0.181	851
473	0.47	2.54	0.307	0.079	0.358	0.264	0.274	851
474	0.47	2.54	0.300	0.079	0.355	0.264	0.274	851
475	0.47	2.54	0.300	0.079	0.355	0.264	0.274	851
458	0.82	12.12	0.810	2.33	0.405	0.09	0.11	851
459	0.82	12.12	0.830	2.33	0.410	0.09	0.11	851
460	0.82	12.12	0.830	2.33	0.410	0.09	0.11	851
404	0.068	7.96	0.96	0.14	2.20	-	-	898
427	0.120	15.3	2.16	1.20	2.12	-	-	898
398	0.18	2.25	0.86	0.14	3.28	-	-	898
334	0.29	2.02	0.78	0.24	2.44	-	-	898
491	0.29	0.98	0.49	0.06	2.91	-	-	898
386	0.329	3.39	0.87	0.28	1.35	-	-	898
383	0.464	4.81	1.21	0.50	1.04	-	-	898
389	0.92	9.42	1.91	1.84	0.55	-	-	898
						-	-	898

To test whether the empirical expression would yield a consistent k_4 at 898°K it was necessary to limit the secondary reaction as much as possible.

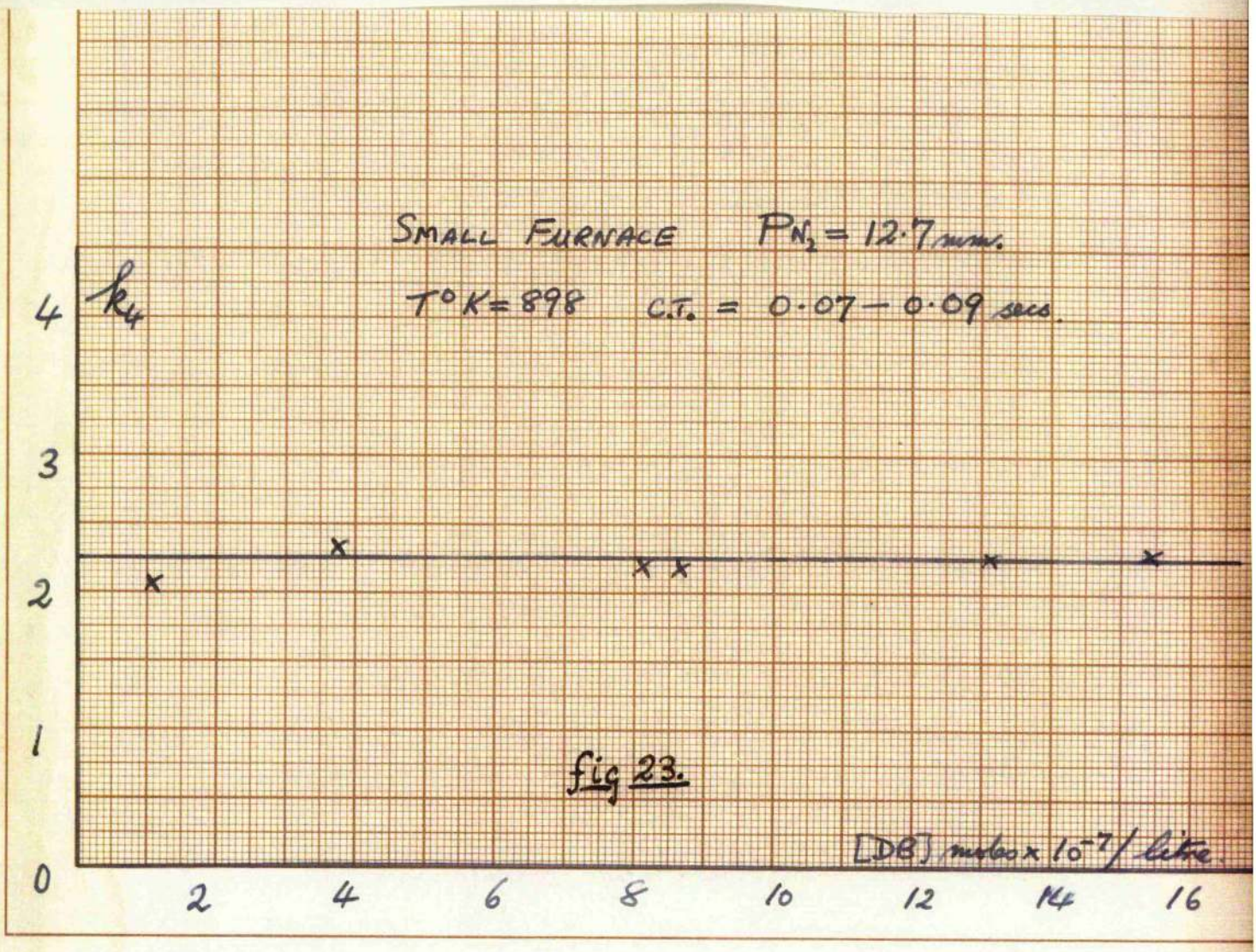

SMALL FURNACE P_{N_2} = 12·7 mms.
T°K = 898 C.T. = 0·07 – 0·09 secs.
k_4
4
3
2
1
0
2
4
6
8
10
12
14
16
[DB] moles x 10^{-7} / litre.

fig 23.

Limitation of secondary effects.

In an attempt to limit the various secondary effects at 898°K a new furnace was installed. (Surface area 441.0 sq.cm., Vol. 36.0 ccs $^{s}/_{v}$ = 12.25 cm^{-1}.). With this new furnace, contact times of 0.06 sec. could be obtained without further modification of the apparatus. It was found possible to prove that with extremely short contact times of the order of 0.06 sec., k_4 was independent of the input concentration of dibenzyl provided the nitrogen pressure was kept constant ($k_4 = \frac{2.3}{t} \text{Log} \frac{a}{(a - y - z)}$ fig.(23))

With this furnace it was impossible to vary the contact time without simultaneously varying the nitrogen pressure, and quite a noticeable pressure effect was observed. A rise with nitrogen pressure had also been observed in values of k_4 determined in the original large furnace, (Runs (340-342) and (392-394)), where it had been possible to keep the contact time constant. The variation in k_4 with nitrogen pressure is plotted in fig.(24).

The data plotted in fig.(23) indicate that at 12.7 mm nitrogen the value of ~~the~~ k_4 for runs completed in the new furnace is of the order of 2.2 $sec.^{-1}$ at 898°K. Using the data in fig.(24) to obtain the value of k_4 for a pressure of 3.9 mm nitrogen we obtain a value of 1.22 $sec.^{-1}$ at 898°K, which is much lower than the maximum limiting value k_4 = 3.65 obtained with the original furnace. The rate of reaction to form iodine has apparently decreased in the smaller furnace to 33.4% of the limiting value in the large furnace.

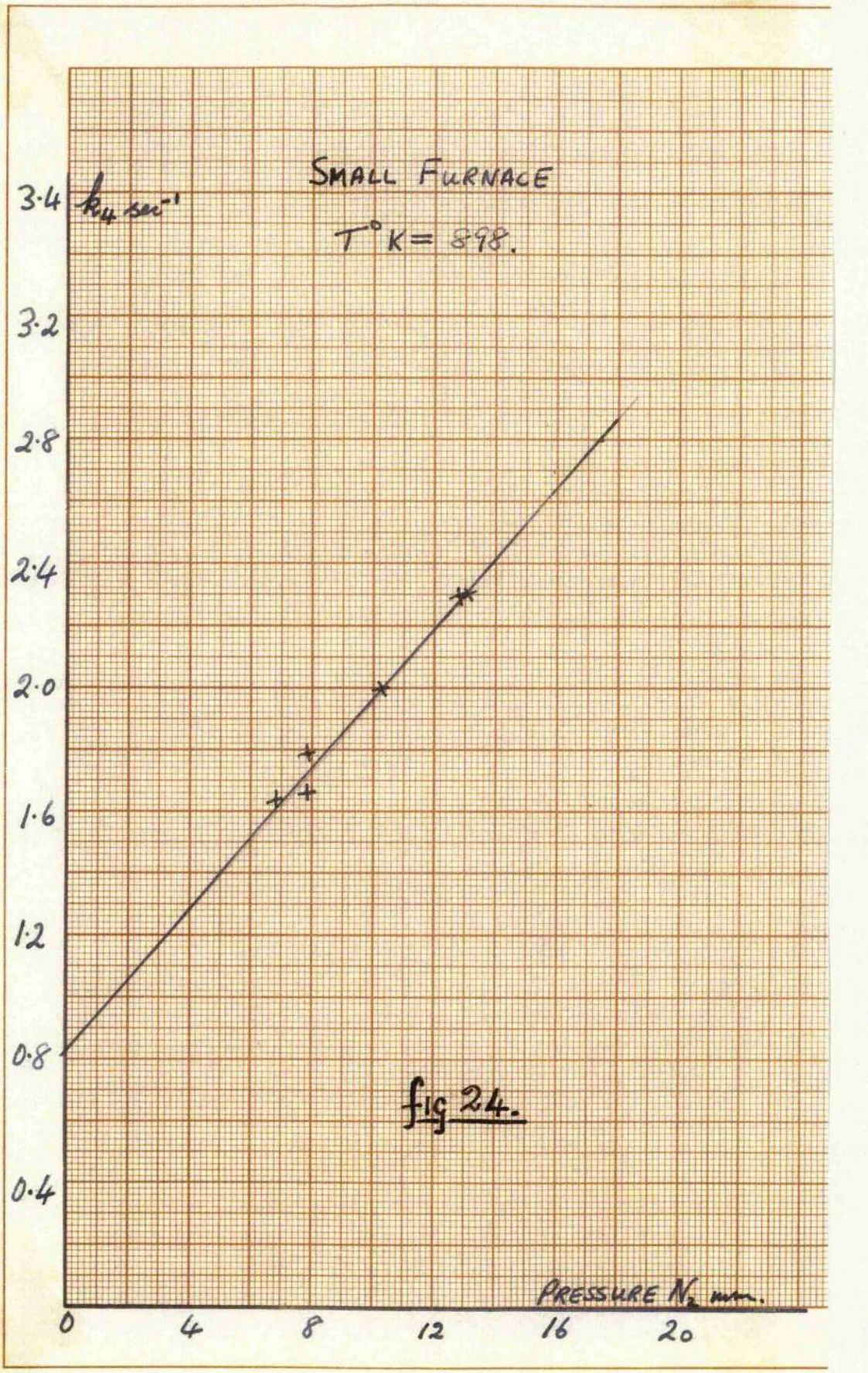

SMALL FURNACE
T°K = 898.
3·4
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
4
8
12
16
20
PRESSURE N₂ mm.

fig 24.

It is possible to explain this behaviour if it can be assumed that benzyl radicals can be stabilized by absorption on the furnace wall. Under these conditions reaction (3a) may take place to an appreciable extent resulting in a lower observed rate of dissociation.

$$C_7H_7\text{-} + C_7H_7\text{-} \longrightarrow C_{14}H_{14}. \quad \ldots\ldots (3a)$$

(94)

According to Hinshelwood, the number of collisions suffered by a molecule in the gas phase before it reaches the wall of the reaction vessel may be roughly estimated by the expression

$$Z = \frac{3\pi\bar{x}^2}{4\,l^2}$$

Where Z = the number of collisions, $\bar{x}$ = the distance in cms between the original position of the molecule and the wall, and l = mean free path. Both furnaces having been constructed with a centrally placed thermocouple tube, consisted essentially of an annular space. The original furnace had the following dimensions:-

Internal Diameter of outer jacket = 2.5 cm.

External " " inner " = 1 cm.

Any molecule placed between these walls must diffuse at least 0.75 cm = $\bar{x}_1$. The corresponding new furnace dimenions were:-

Internal Diameter of outer jacket = 1.30 cm.

External " " inner " = 1.00 cm.

and the minimum distance for diffusion = 0.15 cm = $\bar{x}_2$

Hence

$$\frac{Z_1}{Z_2} = \frac{\bar{x}_1^2}{\bar{x}_2^2} = 25.$$

To a rough approximation a molecule diffusing to the wall in the original furnace would make twentyfive times the number of collisions it would experience in diffusing to the wall of the new furnace assuming both start off mid-way between the inner and outer walls.

In order to obtain a reaction rate such that $k_4 = 3.65$ sec.$^{-1}$ in the new furnace the nitrogen pressure would have to be raised to 25 mm. (fig.24) or by an eightfold factor.

This value agrees reasonably well with the above calculation since at any one temperature the pressure of nitrogen is a direct measure of the concentration of the gas. The number of collisions experienced by a molecule in a single gas varies with the square of the number of molecules per unit volume and therefore with the square of the pressure.

The pressure effect would therefore seem to be explicable as being due almost entirely to the collisions experienced by the molecules diffusing to the walls of the reaction vessels, rather than to any specific difference in the condition of the wall surfaces of the two furnaces. This view is reinforced by the fact that the percentage rise in k_4 is the same in both furnaces for a 100% increase in pressure, e.g.

<u>Original furnace at 898°K.</u>

Runs 340-342. $(DB) = 2.73 \times 10^{-7}$ moles/litre. $k_4 = 2.3$. $PN_2 = 3.81$.

Runs 398-400. $(DB) = 2.25 \times 10^{-7}$ moles/litre. $k_4 = 3.14$. $PN_2 = 7.38$

% increase in pressure = 205%. % increase in k_4 = 136.5%.

<u>From fig(24)</u> for data derived from new furnace.

% increase in pressure = 205%. % increase in k_4 = 132.0%.

The System Dibenzyl and Iodine.

Lack of time limited the extent of the investigations carried out on the reaction between dibenzyl and iodine. The previous qualitative evidence given for this reaction showed the presence of small quantities of hydrogen and toluene in addition to the large quantities of stilbene and hydrogen iodide found in the reaction products. These observations taken in conjunction with the previous general discussion on possible reaction mechanisms lead to the following reaction scheme.

$$C_{14}H_{14} + I \longrightarrow C_{14}H_{13} + HI \quad \ldots\ldots (5)$$

$$C_{14}H_{13} - \longrightarrow C_{14}H_{12} + H \quad \ldots\ldots (6)$$

$$H + I_2 \longrightarrow HI + I \quad \ldots\ldots (7)$$

$$H + HI \longrightarrow H_2 + I \quad \ldots\ldots (8)$$

Secondary reactions

$$C_{14}H_{14} \longrightarrow 2\,C_7H_7 - \quad \ldots\ldots (4)$$

$$C_7H_7 - + HI \longrightarrow C_7H_8 + I \quad \ldots\ldots (2)$$

Step (8) may be dispensed with since at 945°K the quantity of hydrogen iodide was ten times the quantity of hydrogen formed. However the ratio of hydrogen iodide to stilbene is 1 to 1 instead of approximately 2 : 1 expected on the above mechanism (table (23)).

Table (23).

Dibenzyl and Iodine. $P(N_2)$ 3.9 mm.

All concentrations moles x 10^{-7}/litre.

Run No.	C.T. secs.	(DB) IN	(I_2) Mean	(St) Exit	(HI) Exit	$T^{\circ}K$
293	0.28	3.9	11.6	1.99	1.95	809
296	0.27	2.63	12.04	1.06	0.80	851
366	0.26	1.29	9.16	1.11	1.25	898
369	0.26	1.28	4.67	0.94	0.94	898
372	0.26	3.64	3.30	2.11	1.46	898
374	0.27	3.65	3.89	2.30	1.47	898
378	0.26	3.21	9.9	2.99	3.60	898

Below 870°K the rate of dissociation of dibenzyl is quite small and only negligible quantities of toluene would be formed, (none at all at 809°K), therefore the missing hydrogen iodide must be accounted for by some other mechanism. At 898°K where k_4 = 3.65 sec.$^{-1}$ dibenzyl is dissociating quickly, the half life period being of the order of 0.2 seconds, and could account for part of the missing hydrogen iodide by the formation of toluene due to reaction (4) followed by (2).

In fact in the equation

$$-d(C_{14}H_{14})/dt = k_5 (C_{14}H_{14})(2I_2) + k_4 (C_{14}H_{14})$$

there is good evidence for believing that both terms are substantial in magnitude. Since the dissociation process represented by the last term could not contribute to the rate until hydrogen iodide was made available by the attack of iodine atoms, the initial stages might be a case of consecutive reactions. After a reasonable amount of hydrogen iodide had been formed the two processes for removal of dibenzyl could then proceed as concurrent reactions. The difficulty of analysing for dibenzyl has meant that there is no positive evidence on the amount

of residual dibenzyl - if any - issuing from the furnace. In experiments 366 and 378 where the iodine to dibenzyl ratio was highest, the conversion to stilbene is very high, (93% for 366). In such a case it seems reasonable to suppose that, with a high value of k_4, the dibenzyl has probably been completely consumed. Another factor which adds weight to this, and suggests that a similar conclusion may apply to the other experiments at 898°K, is the fact that the variation of iodine concentration by a factor of three (experiments 372 and 378) did not produce a comparable effect on the stilbene production. This could be readily understood if the dibenzyl had been completely removed, by the joint mechanisms discussed, in a period less than the contact time.

If this is so then the ratio of the rate of loss of dibenzyl due to each reaction separately will be given by the expression

$$\frac{(St)}{(2\ \text{toluene})} = \frac{k_5\ 2\alpha I_2}{k_4}$$

If all the dibenzyl is destroyed and we assume there is no back reaction by the toluene and iodine to form stilbene then

$$\frac{(St)}{(DB-St)} = \frac{k_5\ 2\alpha I_2}{k_4}$$

or

$$\frac{k_5}{k_4} = \frac{(St)}{(DB - St)\ 2\alpha I_2}$$

where (St) = stilbene at exit (DB) = input dibenzyl

I_2 = mean iodine concentration.

This method of obtaining k_5/k_4 at 898°K suffers from the fact that in some cases the difference between the input dibenzyl concentration and the exit stilbene is very small and hence the values obtained for k_5/k_4 table (24) show a variation by a factor of two.

Table 24.

Dibenzyl and iodine. $P(N_2)$ 3.9 mm.

All concentrations moles x 10^{-7}/litre.

Run No.	C.T. secs.	(DB) In	(I2) Mean	(St) Exit	(HI) Exit	T°K	k_5 x10^{-7}	$\frac{k_5}{k_4}$ x10^{-6}
366	0.26	1.29	9.16	1.11	1.25	898	0.72	1.98
369	0.26	1.28	4.67	0.94	0.94	898	0.59	1.61
372	0.26	3.64	3.30	2.11	1.46	898	0.39	1.08
374	0.27	3.65	3.89	2.30	1.47	898	0.69	1.85
378	0.26	3.21	9.9	2.99	3.60	898	0.77	2.11

The values in the last column in table (24) can be compared with the value of 2.25×10^6 for the same quantity obtained in the treatment of the system dibenzyl and hydrogen iodide (table (21)). The agreement is good and suggests that the conclusions derived there about the probable energies of activation of the reactions are reasonable.

The second last column lists values of k_5 derived by using the limiting value of k_4 obtained by extrapolation of the results at 898°K in the dibenzyl and hydrogen iodide reaction (fig.21). Taken in conjunction with the value of $k_5 = 0.23 \times 10^7$ at 809°K, they yield an energy of activation in the range 8.5 to 18.5 K cals/mole

There still remains outstanding the question of the missing hydrogen iodide over the entire temperature range. One feature of this

reaction not present in the other systems - toluene-iodine, and dibenzyl-hydrogen iodide - is the immense quantity of dibenzyl radicals present. The speed of the reaction, together with the fact that the dibenzyl concentration is some ten to one hundred times the intermediate concentration of dibenzyl in the toluene-iodine system, and the concentration of iodine is almost one hundred times the iodine concentration found in the dibenzyl-hydrogen iodide system leads to radical concentrations far in excess of those normally encountered in the two systems mentioned (100 to 1000 times).

This fact together with the previous calculations on the possible stability of the dibenzyl radical would suggest that the following process takes place either in the gas phase or possibly to some extent on the wall

$$C_{14}H_{13} + C_{14}H_{13} \longrightarrow 2\,C_{14}H_{12} + H_2.$$

In this manner molecular hydrogen could be formed in concentrations up to fifty per cent of the total hydrogen iodide concentration, e.g.

$$2\,C_{14}H_{14} + 2I \longrightarrow 2\,C_{14}H_{12} + 2HI + H_2.$$

This reaction would be most effective at the lower temperatures where the stability of the dibenzyl radical is enhanced. Unfortunately the only hydrogen analysis was obtained from a run done at 945°K where very considerable dissociation of the dibenzyl takes place and under these conditions it is not surprising that the hydrogen analysis yielded only ten per cent molecular hydrogen compared to the hydrogen iodide concentration.

The System Toluene and Iodine.

The reaction scheme devised in the early stages of these investigations and presented in fig. (17) showed the process - $C_7 H_8 + I \rightarrow C_7 H_7^- + HI$. In the later work on the reactions of dibenzyl with iodine and hydrogen iodide there has been ample evidence of the speed and extent of the reverse reaction in the above equation and this was the reason for the approximate calculation of the position of possible equilibrium which might be reached if radical dimerisation did not remove the benzyl radicals.

In the initial treatment of the scheme of fig. (17), it was not visualised that the possibility of a state of near equilibrium could arise from reactions (1) and (2) under the experimental conditions used and the system was treated as a normal case of partial inhibition by products. It was from this point of view that the data of table (14) were viewed, where it was shown that added hydrogen iodide depresses its own yield by reaction (1). However such data could also be explained by displacement of an equilibrium which was then frozen at the exit of the furnace.

At first sight it seems that the classical method of distinguishing a rate process from an equilibrium should be applied - to study the variation in behaviour with time as well as with concentration. It was not possible to do this within the period of this work but, because of the subsequent reactions (4) and (5), and the fact that the latter produces hydrogen iodide, it would not be possible to use the hydrogen iodide production as an index of reaction rate in (1) and (2) unless all other products were considered as well. If reaction times of toluene and iodine are increased we undoubtedly

get eventually a complete conversion to stilbene and hydrogen iodide. Thus the effect of the time variable is not simple.

Since this criterion, if applied, will certainly not settle the problem it will be necessary to consider some of the facts shown by the existing data.

In the first place it is seen that the data shows the reaction of dibenzyl and iodine at 809 - 945°K results in a rapid production of stilbene. Now at 809°K for the system toluene and iodine the stilbene issuing from the furnace is negligible (expts. 217,218) although the iodine concentration is substantial and appreciable hydrogen iodide has been formed. The only reasonable conclusion appears to be that the benzyl radicals formed by (1) had not dimerised in the furnace. In such experiments the hydrogen iodide stilbene ratio is about 51.7:1 showing that the other product is dibenzyl.

Now the dissociation of dibenzyl would not produce as high a concentration of benzyl radicals at 809°K, but those which are produced react quickly with the added hydrogen iodide to yield iodine. It seems reasonable to suppose therefore that reaction (2) is important even as low as 809°K. Moreover reaction (2) would appear to be faster under the concentrations used than the dimerisation of benzyl radicals to form dibenzyl. If this were not so the kinetics of the dibenzyl-hydrogen iodide system would have been markedly different.

At 898°K in the dibenzyl and hydrogen iodide reaction the conversion of dibenzyl as judged by iodine production reached 62.5 per cent.

The data for these experiments fall in with the kinetic analysis made for the other conditions and suggest that the equilibrium position for reactions (1) and (2) lies well to the left of the equation

$C_7 H_8 + I \longleftrightarrow C_7H_7 + HI.$

If this is the case then it should be possible to attempt to calculate equilibrium constants for the toluene and iodine mixtures rather than rate constants. Such constants cannot be exact as it is known that (4) and (5) are proceeding as side reactions, but if the speeds of (1) and (2) are as high as the above arguments suggest then approximate values of K eq might result.

The experimental data have been treated at 945°K on the following lines. The hydrogen iodide and iodine concentrations in the equilibrium constant $K(eq) = \frac{(C_7 H_7)\ (HI)}{(C_7 H_8)\ (I)}$ are taken as the exit values from the furnace. The $(C_7 H_7)$ was derived as the equivalent of (HI at exit - 4x stilbene at exit), while the toluene concentration at the exit was the input figure less the concentration of benzyl radicals at the exit together with twice the exit concentration of stilbene.

It is a well known difficulty in the evaluation of equilibrium constants that errors in analyses have a serious effect on final calculated constants, because under-estimation of one quantity results as a rule in over-estimation of another. Such troubles will obviously beset the estimations made here and in view of this and the range of concentrations employed the results in Table (25) are very encouraging. Taking a value of $K_{eq} = 0.0156$ at 945°K one deduces ΔG° for the process as 7,820 calories.

From previous arguments (p.98) it has been seen that the entropy change in this reaction is about 9.83 eu. at 945°K. We can therefore deduce a ΔH° value of 17.15K cals.

In order to deduce a value for the bond dissociation of toluene we note that this means (D (Ph CH_2- H) - D(H - I)) at 945°K = 17.15, and we can therefore evaluate D (Ph CH_2- H) at this reaction temperature, or we can attempt to correct the heat of reaction to 298°K.

Taking the data from "Selected Values of Chemical Thermodynamic Properties" N.Bur.Std. Circular 500 we find D (H - I) at 945°K = 73.3 thus making D (Ph CH_2- H) at 945°K = 90.45K cals. To compare this value with the data of other workers we have to correct to 298°K the heat of reactions for Ph CH_3 $\longrightarrow$ Ph CH_2 + H. Assuming that the specific heat of toluene and the benzyl radical are the same to a first approximation we have ΔC_p = 4.97 and hence D (Ph CH_2 - H) at 298°K = 90.45 - 3.22 = 87.23K cals. Clearly the alternative method indicated will give the same result if the same assumptions are made.

It is difficult to assess the accuracy of this result since there are two major uncertainties which influence the calculation of ΔG°. Equilibrium may not be fully attained due to the dimerisation of radicals being of minor, but significant, importance. Moreover the assumption of the stoichiometric calculations has been that the concentration of free dibenzyl was negligible. If the first assumption was incorrect we would have too low a value for the equilibrium radical concentration being used in calculations while the second assumption would cause the opposite state of affairs.

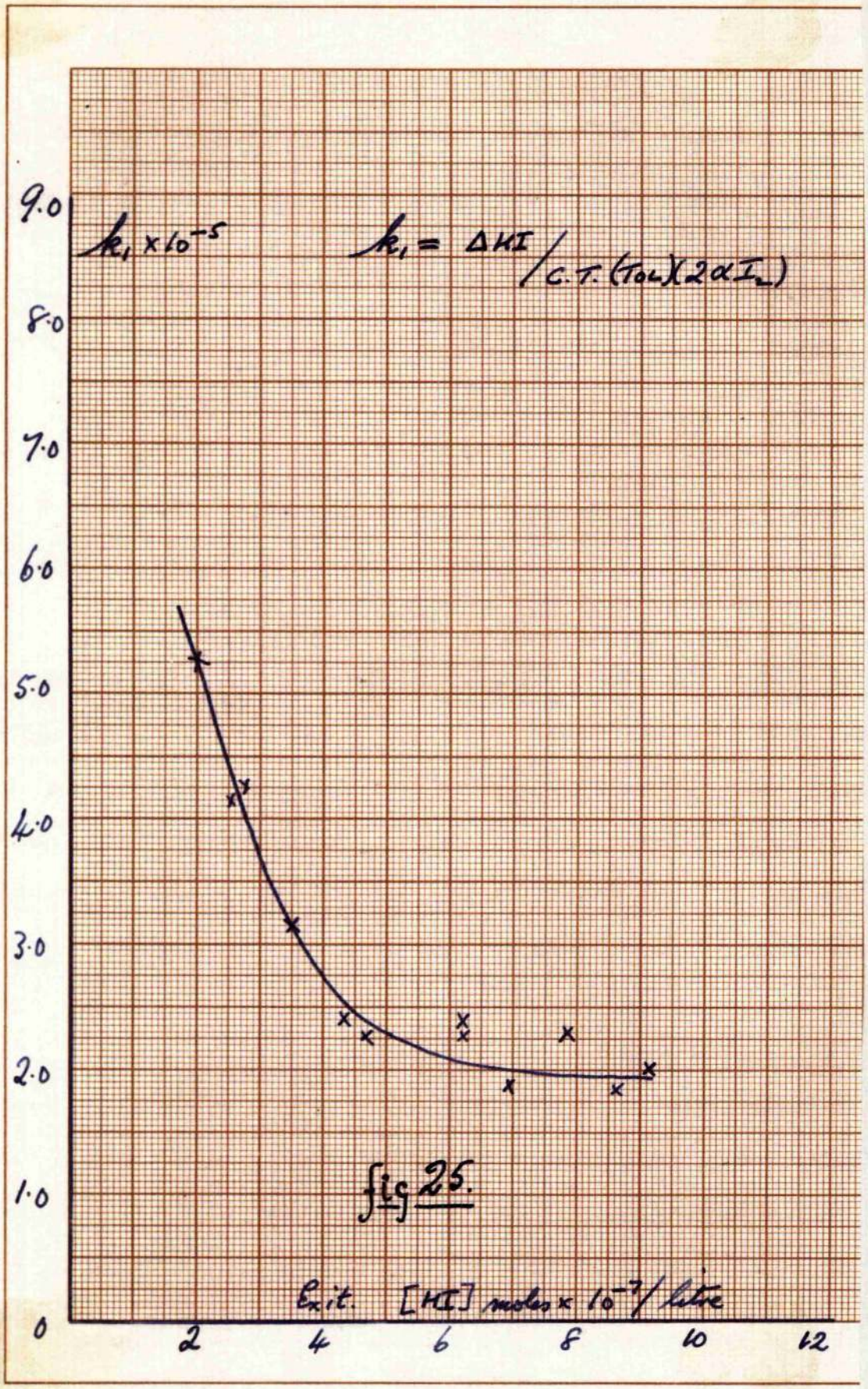

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
$k_1 \times 10^{-5}$
$k_1 = \Delta HI / c.t.(Tol)(2\alpha I_2)$
2
4
6
8
10
12
Ext. [HI] moles $\times 10^{-7}$ / litre

fig 25.

Table (25)

Equilibrium Constant K (eq.)

Toluene and Iodine $P(N_2)$ 3.9 mm. All concentrations moles x 10^{-7}/litre.

Run No.	T°K	(Tol) exit	($2aI_2$) exit	(HI) exit	(St) exit	K(eq.)	ΔG° K cals	ΔS° e.u.	T. ΔS° K cals	ΔH° K cals
188-189	968.5	30.9	15.5	5.02	1.03	0.01915	7.62	9.89	9.58	17.2
196-198	962.5	31.4	8.33	2.86	0.67	0.0201	7.48	9.87	9.50	16.98
193-195	957.	31.6	13.43	4.30	0.91	0.0218	7.26	9.86	9.43	16.69
199-201	951.	30.9	14.28	4.47	0.98	0.0177	7.62	9.85	9.38	17.0
256-258	945.	30.95	34.0	7.75	1.60	0.0156	7.82	9.83	9.28	17.10
259-261	945.	21.3	49.2	10.5	2.26	0.0150	7.86	9.83	9.28	17.16

No attempt was made to extend this treatment to data obtained below 945°K. No account has been taken of the small quantities of molecular hydrogen found during runs. If such hydrogen is produced instead of hydrogen iodide in the formation of stilbene, as seems quite likely, then the benzyl radical concentration may be lower than indicated above. This would in turn lead to a higher value for ΔH°.

Calculation of a rate constant.

The calculation of a rate constant for step one involves a knowledge of the hydrogen iodide produced directly by the interaction of toluene and iodine. It has already been pointed out that at 945°K the ratio of hydrogen iodide to stilbene is approximately 4 : 1 and this together with the data on

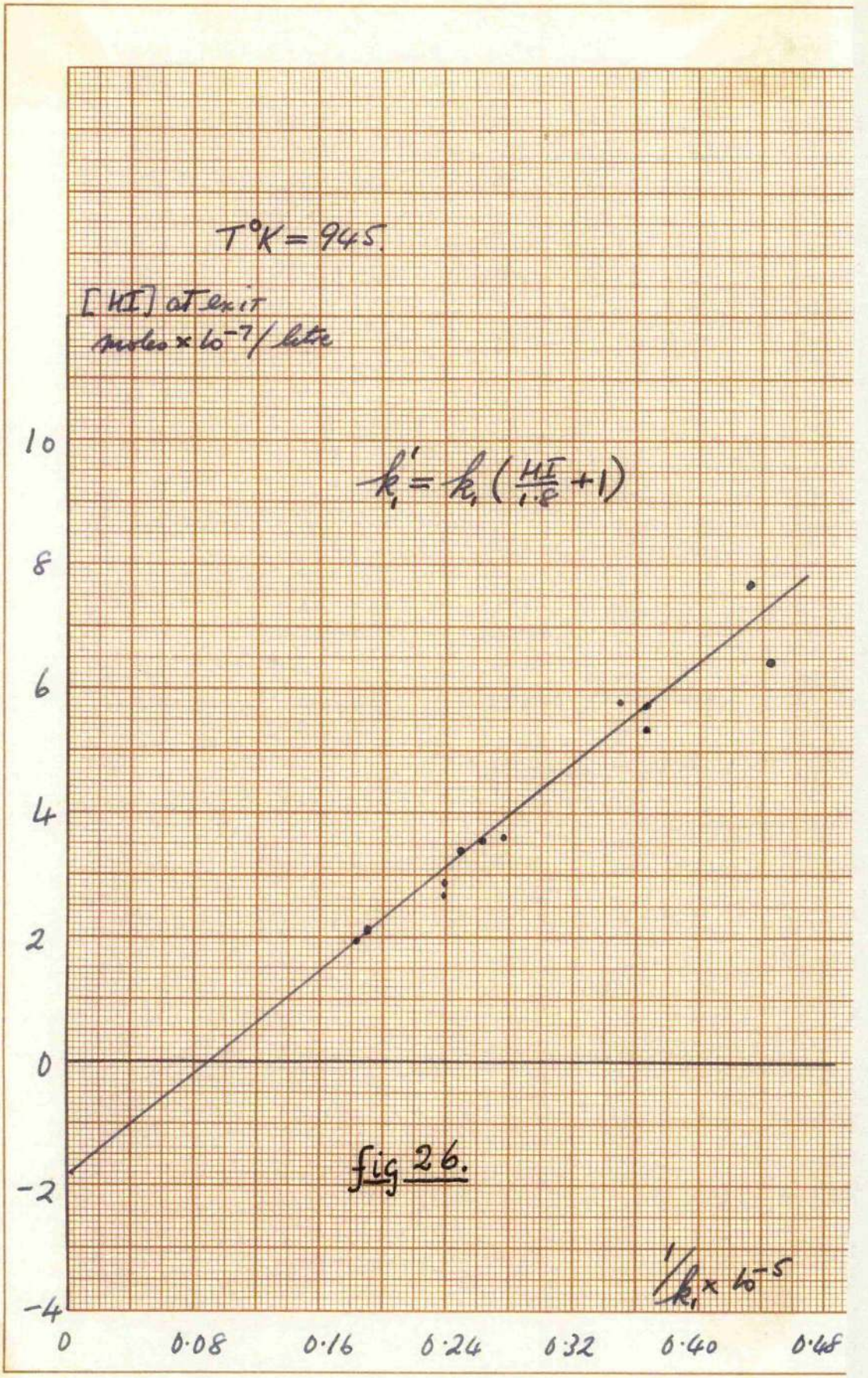

$T°K = 945.$
[HI] at exit
moles × 10^{-7} / litre
$k_1' = k_1\left(\frac{HI}{1.8} + 1\right)$
10
8
6
4
2
0
-2
-4
0
0·08
0·16
0·24
0·32
0·40
0·48
$\frac{1}{k_1} \times 10^{-5}$

fig 26.

the dibenzyl-iodine system, in which at this temperature all dibenzyl present as such is converted into stilbene, suggests that the hydrogen iodide due to the initial reaction between toluene and iodine may be calculated as the difference between the hydrogen iodide total and twice the stilbene produced.

On this basis the following rate constant was evaluated for the data at 945°K.

$$\Delta HI = HI \text{ total} - 2 \text{ stilbene}$$

$$K_1 = \Delta HI / C.T. \ (C_7 H_8)(2aI_2)$$

where C.T. = contact time in seconds.

A plot of K_1 versus the total hydrogen iodide concentration at the exit is given in fig. (25), which shows that values of K_1 increase markedly as the hydrogen iodide exit concentration falls. This is to be expected on the previous evidence for inhibition and the data on the dibenzyl-hydrogen iodide system.

In order to determine the initial rate constant, K_1^{it} would be ideal to plot K_1 versus the hydrogen iodide exit concentration and extrapolate this curve to zero exit concentration of hydrogen iodide. This in practice proved rather difficult due to the hyperbolic nature of the curve at small exit concentrations of hydrogen iodide (fig.25) and instead the plot of $\frac{1}{K_1}$ versus the total exit hydrogen iodide concentration was extrapolated (fig.26).

Under these conditions we have

$$\frac{1}{K_1'} = \frac{1}{K_1 \left(\frac{HI}{C} + 1\right)}$$

$$\text{or} \quad K_1' = K_1 \left(\frac{HI}{C} + 1\right)$$

From fig. (26) $K_1^1 = 11.4 \times 10^6$.

$\therefore \text{Log}_{10} K_1' = 7.06.$

If we assume $A_1 = 10^{11}$ mole^{-1} litre sec^{-1}

we have $7.06 = 11 - E_1/4,400$

or $E_1 = 17.3$ K cals.

$\therefore$ D (Ph CH_2 - H) = 88.3 K cals/mole.

This is remarkably close to the value of 87.3 K cals/mole determined from equilibrium data at high exit concentrations of hydrogen iodide.

General Conclusions on Some bond dissociation energies.

The data which have been presented show a considerable measure of support for a $D(PhCH_2 - H)$ value of 87 ± 2 K. cals/mole. This is distinctly higher than the value of 77.5 k. cals deduced by Szwarc from the pyrolysis of toluene and lies in between the values quoted by Van Artsdalen and Benson of 89.9 and 84 respectively. Since we have had to establish the main features of a series of interlocking reactions the data have not always been obtained under the best possible conditions for evaluation of these thermal quantities. For example the dibenzyl + iodine investigation might profitably be extended to a lower temperature range in order to obtain E_5 with accuracy. If more data were available for reaction systems and conditions where only small percentage conversions occur then more accurate velocity constants might result.

But taken as a whole the results are consistent within themselves and in reasonable agreement with expectations for the types of reaction involved.

Summary.

1. The thesis contains an account of work which began by a study of the gaseous reaction of toluene and iodine and developed into a study of two additional systems:-

(a) dibenzyl and hydrogen iodide,

(b) dibenzyl and iodine.

2. The observations on these systems are explained in terms of the general scheme.

$$C_6H_5CH_3 + I \underset{(2)}{\overset{(1)}{\rightleftharpoons}} C_6H_5CH_2 - + HI$$

$$C_6H_5CH_2 - \underset{(3)}{\overset{(4)}{\rightleftharpoons}} C_6H_5CH_2CH_2C_6H_5$$

$$C_6H_5CH_2CH_2C_6H_5 \xrightarrow{(5)} C_6H_5CH = CHC_6H_5 + 2HI.$$

The reaction (5) is discussed in terms of a two stage process caused by iodine atom attack and going through the intermediate formation of the $Ph.C_6H.CH_2.Ph$ radical. The decomposition of this can, in suitable conditions, produce hydrogen.

3. The reactions have been studied in flow systems with reaction times of 0.07 to 0.92 seconds, at temperatures of 809 - 968°K, with carrier gas pressures of 3 to 15 mm. and reactant concentrations in the region 1 to 40 x 10^{-7} moles per litre.

Reactants were injected into the carrier gas and products frozen out from it and analysed by titration, U.V. absorption, spectrophotometry and mass spectrometry.

4. Dibenzyl and hydrogen iodide.

The reaction forms iodine, stilbene, hydrogen and toluene, and its rate is independent of the concentration of hydrogen iodide for appreciable values of the latter.

The kinetics are explained on the basis of a slow dissociation process (4) in the above scheme, followed by a rapid reaction (2). As iodine is formed process (5) enters as a concurrent reaction. The hydrogen is ascribed to the process Ph C-H CH_2 Ph $\longrightarrow$ Ph CH = CH Ph + H followed by a substantial amount of the process H + HI $\longrightarrow$ H_2 + I.

Kinetic analysis of the competing processes for dibenzyl removal has given values of (k_5/k_4) at various temperatures, from which we obtain $(E_5 - E_4) = -47$ k. cals.

By using initial rate conditions as far as possible values of k_4 at various temperatures have been deduced and lead to $\log_{10}k_4 = 15.4 - (61{,}000/4.57T)$.

Using the latter data we obtain $\log_{10}k_5 = 10.2 - (14{,}000/4.57T)$.

It is suggested that the 61 k. cals. can be ascribed to the bond dissociation energy for the central (C - C) bond in dibenzyl, and that the 14 k.cals. is the energy of activation for abstraction of a secondary hydrogen atom by an iodine atom. This places the strength of such a (C - H) bond at a maximum of 85 k. cals.

5. Dibenzyl and iodine.

Investigations were confined to the same temperature range as required for reactions (1) and (4) in order to supplement the data on those processes. This process proved very rapid in such conditions

and E_5 was not deduced with accuracy but was assessed as being in the region 8.5 to 18.5 k. cals.

6. Toluene and iodine.

The complications in this reaction are greater as seen in the above scheme.

At 945° a study was made of the marked inhibition by hydrogen iodide through reaction (2) and an extrapolation method used to deduce an initial rate constant. Assuming a temperature independent factor of 10^{11} for process (1) a maximum value of 88 k. cals was obtained for the dissociation energy ($PhCH_2$ - H).

For conditions where more extensive reaction occurs a treatment of the data has been applied which assumes an approach to equilibrium has been achieved in the system $PhCH_3 + I \longleftrightarrow PhCH_2 + HI$.

Thermodynamic arguments suggest such an equilibrium mixture will contain an excess of toluene and iodine, and using an approximate value for the entropy of the benzyl radical with a determined ΔG° we have obtained ΔH° at 945° = 17.1 k. cals. This places the value of D($PhCH_2$ - H) for that temperature at 88 k. cals.

7. The results obtained suggest that D($PhCH_2$ - H) is certainly not as low as the 77.5 k. cals given by Szwarc and after correction to 298°K, it is considered to be about 85 - 88 k. cals. This places it between Van Artsdalen's value of 89.9 k.cals and Benson's of 84 k. cals.

8. Surveys of relevant literature and suggestions for further work are given.

Appendix (1)

Calculation of vapour pressure of stilbene, and hence the approximate correction to be applied to experimental results obtained with trap maintained at 20°C.

Melting point = 124°C = 397°K (Handbook of Chem. and Physics.)
Boiling point = 307°C = 580°K (" " " " ")

From Trouton's Rule:

$L(v) = 22.5 \times 580 = 13.05$ K cals.

$L(f) = 30.2$ K, joules $= 30.2 \times 0.2392$ K cals $= 7.22$ K cals. (I.C.T.)

Hence $L(s) = 20.25$ K cals.

Let the vapour pressure at the melting point be p, then:

$\log_{10}(760/p) = 13050 \times 183 / 4.57 \times 580 \times 397$. (Clausius Clapeyron Equation)
$= 2.26$

$\log_{10} p = 2.8808 - 2.26 = 0.62$

and vapour pressure = 4.17 mm Hg.

If we let the saturated vapour pressure of stilbene at 20°C = y, then:

$\log_{10}(4.17/y) = 20250 \times 104 / 4.57 \times 397 \times 293 = 3.96$

$\log_{10} y = 0.62 - 3.96$.

$y = 4.57\ 10^{-4}$ mm

During a typical run the conditions are approximately as follows:-

Average furnace exit pressure of nitrogen = 3.92 mm Hg.

Average rate of flow of nitrogen = 80.0×10^{-6} moles/sec.

Hence average rate of flow of stilbene = $(4.57/3.92) \times 80 \times 10^{-10}$.
$= 9.33 \times 10^{-9}$. moles/sec.

Note, the experimentally derived value of $L(s) = 21.7$ K cals, obtained by Weghofer and Wolf, (Z, Phys Chemie, 3, 39-40, 1938) is only 6% greater than the above theoretical value.

Appendix (2)

Calculation of the vapour pressure of dibenzyl in order to estimate whether any dibenzyl would in fact be removed from the carrier gas stream under normal flow conditions in a trap maintained at 20°C.

Melting point = 52°C = 325°K. (Handbook of Chem. and Physics.)

Boiling point = 284°C = 557°K.(" " " " ")

L(f) = 23.64 K joules = 23.64 x 0.2394 K cals/mole = 5.655 K cals/grm.mole (International Critical Tables).

L(s) = 17.5 K cals/mole (Weghofer and Wolf).

By Trouton's Rule:-

$L(e) = 22.5 \times 557 = 12.53$ K cals/mole, or $L_s - L_f = 17.5 - 5.66 = 11.84$.

Now at the melting point both the solid and liquid forms are in equilibrium and have the same vapour pressure, hence:-

$$\log (760/p) = \frac{125.30 \times 232}{4.57 \times 557 \times 325}$$

$$= 3.53$$

Hence $\log p = 2.8808 - 3.53$

$= \bar{4}.47 + 2.8808$

$= \bar{1}.35$

$p = 0.22$ mm Hg.

If we let the saturated vapour pressure of dibenzyl at 20°C equal y then:

$$\log (0.22/y) = \frac{1819 \times 32.}{4.57 \times 325 \times 293.}$$

$$= 1.337.$$

$\log y = \bar{2}.03$

$y = 0.01$ mm Hg.

During a typical run the conditions are approximately as follows:-

Average furnace exit pressure of nitrogen = 3.92 mm Hg.

Average rate of flow of nitrogen = 80.0×10^{-6} mols/sec.

Hence average rate of flow of dibenzyl = $\frac{1 \times 10^{-2}}{3.92} \times 80.0 \times 10^{-6}$.

$= 2.04 \times 10^{-7}$ moles/sec.

Appendix (3)

Calculation of the half life period of benzyl iodide at 800°K.

According to Szwarc the dissociation of benzyl iodide is a unimolecular reaction and the rate constant may be approximately obtained by means of the equation:-

$$k\,(sec^{-1}) = 10^{13}\ exp\,(-E/RT.)$$

where E = 29.5 K cals/mole.

Hence at 800° K

$$\log_{10} k = 13 - 29.5 \times 1.25/4.57.$$

$$= 13.0 - 8.06$$

$$= 4.94$$

$$k = 9.7 \times 10^{+4} sec\ -1.$$

$$T_{1/2} = 0.69/9.7 \times 10^{+4} = 7.1 \times 10^{-6} \text{ seconds.}$$

Accordingly at 800°K any benzyl iodide formed inside the furnace would be instantly dissociated.

Appendix (4)

Furnace Data.

Large Furnace.

Volume (V) = 297.75 ccs.

Surface Area (S) = 664.54 sq.cm.

Ratio S/V = 2.23 cm^{-1}.

$$\text{Contact Time} = \frac{4.773 \times 10^{-5} \times P.}{T^{\circ}K \times R_N} \text{ seconds.}$$

P = average pressure in furnace in mm.

R_N = Rate of flow of nitrogen grm moles per sec.

Small Furnace.

Volume (V) = 36 ccs.

Surface Area (S) = 441.0 sq.cm.

S/V = 12.25 cm^{-1}.

$$\text{Contact Time} = \frac{0.569 \times 10^{-3} \times P}{T^{\circ}K \times R_N} \text{ seconds.}$$

Appendix (5)

Thermal data and calculations not included in the main section of the thesis.

Heats of formation.

Dibenzyl $C_{14}H_{14}$.

Heat of combustion = 1805.7 ± 0.3 K cals/mole.

(Coops at alii Rec Trav Chem. 65, 128, 1946)

$$C_{14}H_{14(S)} + 17\tfrac{1}{2}\,O_2 \longrightarrow 14CO_2 + 7H_2O_{(l)} + 1805.7 \qquad (a)$$

$$14\,C_{(S)} + 14\,O_2 \longrightarrow 14CO_2 + 1316.7$$
$$7H_2 + 3\tfrac{1}{2}\,O_2 \longrightarrow 7H_2O_{(l)} + 478.24$$

} Nat. Bur. Standards Circular No.500 (1952)

$$14\,C_{(S)} + 7H_{2R(G)} + 17\tfrac{1}{2}\,O_{2(G)} \longrightarrow 14CO_{2(G)} + 7H_2O_{(l)} + 1794.94 \qquad (b)$$

$$14\,C_{(S)} + 7H_{2(G)} \longrightarrow C_{14}H_{14(S)} - 10.76 \qquad (b - a).$$

The latent heat of fusion of dibenzyl = 31 cals/grm = 5.64 K cals/mole.

(Hand Book of Chemistry and Physics).

$\log_{10}p$ versus $I/T^{\circ}K$ plot of the vapour pressure data of dibenzyl. (Stull Ind.Eng.Chem., 39,517 - 540, 1947) gives a value of 13.3 K cals/mole for the latent heat of evaporation.

$$C_{14}H_{14(S)} \longrightarrow C_{14}H_{14(G)} - (13.3 + 5.64)\text{ K cals.}$$

$$14\,C_{(S)} + 7H_2 \longrightarrow C_{14}H_{14(G)} - 29.7\text{ K cals. at } 25^{\circ}C.$$

$$\Delta H^{\circ}_{f_{298}} = 29.7\text{ K cals/mole.}$$

Stilbene (Trans)

$$C_{14}H_{12(S)} + 17O_2 \longrightarrow 14CO_2 + 6H_2O_{(l)} + 1758.8 \qquad (c)$$

(data of Richardson & Parks J.A.C.S 61, 3543-6 1939)

and, as previously

$$14\,C_{(S)} + 6H_2 + 17.0_2 \longrightarrow 14\,CO_2 + 6H_2O_{(l)} + 1726.62 \qquad (d)$$

$$14\,C_{(S)} + 6H_2 \longrightarrow C_{14}H_{12(S)} - 32.18.$$

Latent Heat of fusion = 39.9 cal/grm.

= 7.18 K cals/mole. (Hand Book Chem.& Physics).

Vapour Pressure data quoted by Stull yield a latent heat of vaporisation L_V = 14.95 K cals/mole.

$$C_{14}H_{12(S)} \longrightarrow C_{14}H_{12(G)} - 22.13 \text{ K cals.}$$

$$14\,C_{(S)} + 6H_2 \longrightarrow C_{14}H_{12(G)} - 54.31.$$

$$\Delta H^{\circ}_{f298} = 54.31.$$

Toluene.

A.P.I. Tables list ΔH°_{f298} toluene = 11.95 K cals.

The above heats of formation allow the thermochemistry of various conceivable processes to be estimated for the decomposition of dibenzyl into complete molecules.

(1) $C_{14}H_{14(G)} \longrightarrow C_{14}H_{12(G)} + H_2$ ΔH° = 24.61 K cals/mole.

(1a) $C_{14}H_{14(G)} \longrightarrow C_{14}H_{12(G)} + 2H$ ΔH° = 127 K cals/mole.

(2) $C_{14}H_{14(G)} \longrightarrow 2\,C_7H_8 + C_{14}H_{12}$ ΔH° = 18.81 K cals/mole.

In both cases these reactions are endothermic.

Assessment of the heats of formation of the benzyl and dibenzyl radicals.

(a) $C_{14}H_{14(G)} \longrightarrow 2\ Ph\ CH_{2(G)}$

The thermal value of this reaction depends on the heat of formation of Ph CH_2. This in turn may be calculated if the strengths of any of the bonds of type (Ph CH_2-X) are known.

Estimates of the (C-H) bond strength in toluene range from 77.5 to 89.0 K cals/mole.

$$Ph\ CH_2\text{-}H \longrightarrow Ph\ CH_2\text{-} + \text{-}H \qquad 77.5 - 89\ K\ cals.$$

and ΔH° reaction = ΔH_f° Ph CH_2- + 52 — $\Delta H_f^\circ\ C_7H_8$.

If ΔH° = 77.5 or 89 K cals.

$$\Delta H_f^\circ \text{ Ph } CH_2\text{-} = 57.45 \text{ or } 49.45.$$

This in turn yields a value for the change in heat content in the reaction

$$C_{14}H_{14\,(G)} \longrightarrow 2\ C_7H_7\text{-}$$

of 45.2 or 69.2 K cals/mole.

Thermodynamic Data on intermediate reactions involving radicals.

(b) Ph CH_2- + Ph-CH_2-CH_2-Ph Ph CH_3 + Ph - $\underset{|}{CH}$ - CH_2 - Ph.

We may estimate the change in heat content in this reaction as the difference in the abstraction of a secondary hydrogen to form a primary carbon-hydrogen bond. The reaction will therefore be about 7 K cals ex othermic. If we use one of the listed values for the

toluene (C - H) bond dissociation energy and the corresponding value for the heat of formation of the benzyl radical together with the heat of formation of dibenzyl we find

$$\Delta H_f^\circ \text{ Ph-}\underset{|}{\text{CH}}\text{-}\underset{2}{\text{CH}}\text{- Ph} = 37.45 + 29.7 - 11.95 - 7$$

$$= \underline{48.2 \text{ K cals.}}$$

This value together with the heats of formation of dibenzyl and stilbene allow us to deduce ΔH_f° values for the following steps

(c) $\text{Ph-}\underset{|}{\text{CH}}\text{-}\underset{2}{\text{CH}}\text{- Ph} \longrightarrow \text{Ph CH = CH Ph} + \text{H} - 58.2 \text{ K cals.}$

(d) $2(\text{Ph-}\underset{|}{\text{CH}}\text{-}\underset{2}{\text{CH}}\text{- Ph}) \quad \text{Ph CH = CH Ph} + \text{Ph-}\underset{2}{\text{CH}}\text{-}\underset{2}{\text{CH}}\text{- Ph} + 12.4 \text{ K cals.}$

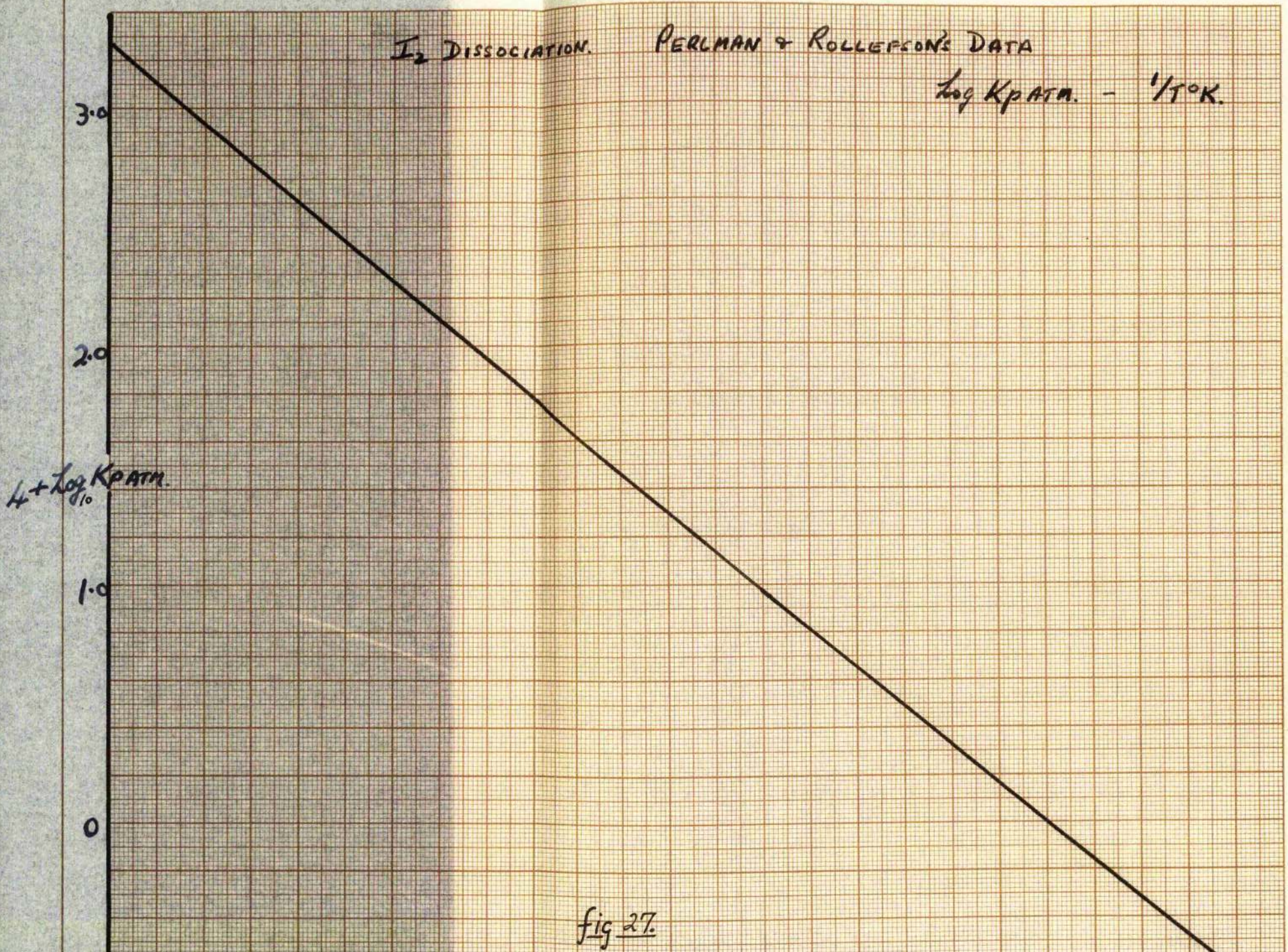

I_2 Dissociation. Perlman & Rollefson's Data
Log Kp atm. - 1/T°K.
3.0
2.0
4+Log10 Kp atm.
1.0
0

fig 27.

Appendix (6)

The dissociation of iodine.

$$I_2 \longrightarrow I + I.$$

Let c = concentration of iodine in moles/litre

and a = the fraction dissociated.

Then $\frac{a^2 c}{(1-a)} = K_c$ (1)

Now $K_p = K_c\ RT^{\Delta N}$ where in this case the dissociation of a molecule into two particles, $\Delta N = 1$.

$$\log_{10} K_p = \log_{10} K_c + \log_{10} RT \quad (K_p \text{ units in atmospheres}).$$
$$= \log_{10}\frac{a^2}{(1-a)} + \log_{10} C + \log_{10} RT \qquad (2)$$

The most accurate data for the dissociation of iodine is due to Perlman and Rollefson (J. Chem. Phys. 367 1941) (fig.27).

The following values of $\log K_p$ v $1/T^{\circ}K$ have been abstracted from this paper

$T^{\circ}K$	800	840	880	920	960
$1/T \times 10^3$	1.25	1.19	1.136	1.087	1.042
$4+\log_{10}Kp$	-0.58	-0.09	+0.35	+0.76	1.13
Therefore					
$\log_{10} K_p$	-4.58	-4.09	-3.65	-3.24	-2.87
RT=0.082T	65.6	68.9	72.2	75.5	78.7
$\log_{10}RT$	1.817	1.838	1.858	1.878	1.896
(LogKp-LogRT)	-6.397	-5.928	-5.508	-5.118	-4.766

From equation 2 we have

$$\log_{10}\frac{a^2}{(1-a)} = \log_{10} K_p - \log_{10} RT - \log_{10} C. \qquad (3)$$

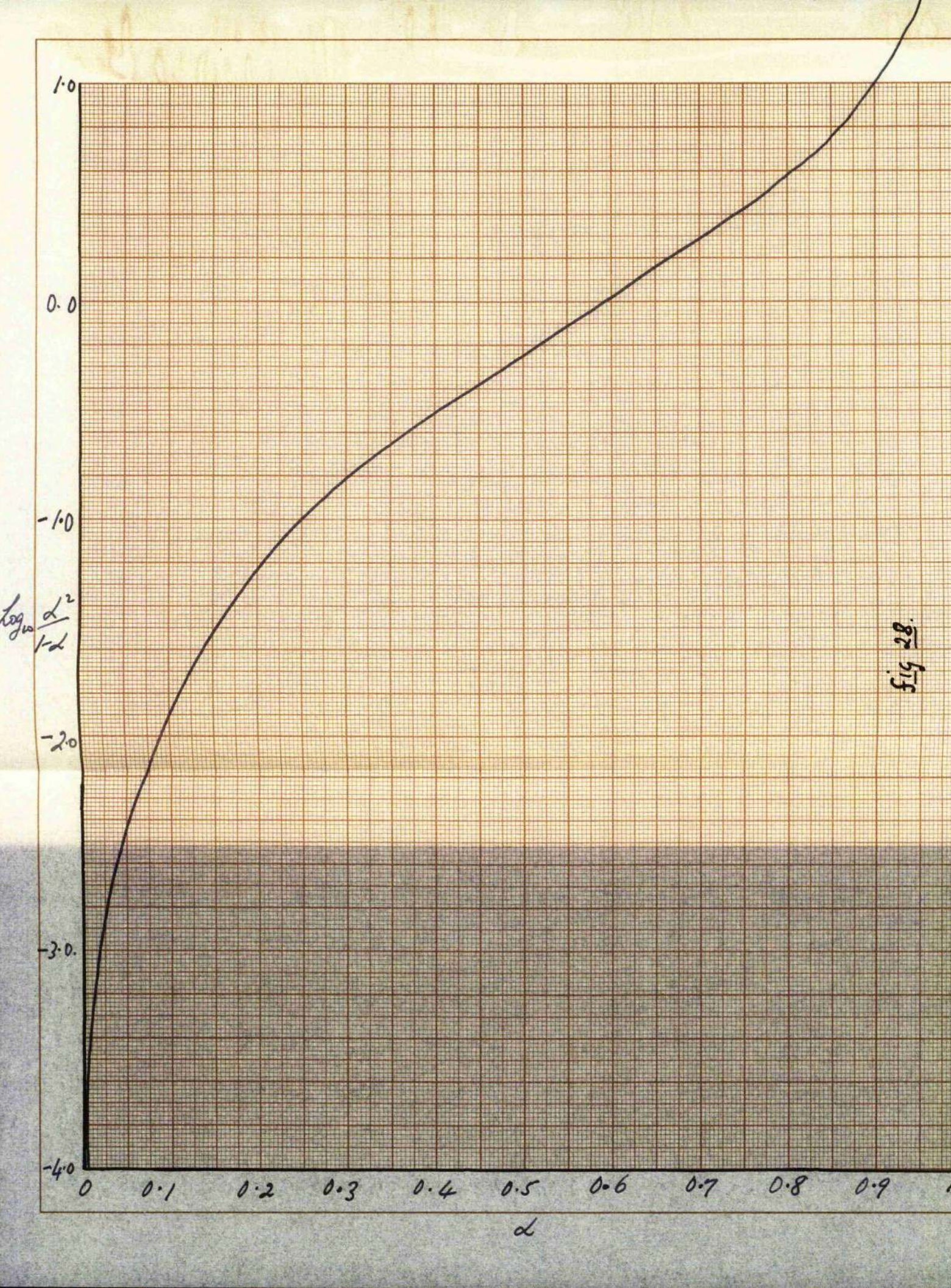

1·0
0·0
-1·0
-2·0
-3·0
-4·0
$\log_{10}\frac{\alpha^2}{1-\alpha}$
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
α

Fig. 28.

To obtain values of a, appropriate values of c (10^{-6}-10^{-8}) were selected and used to solve equation (3) for values of a.
The separate values of a for the various conditions are derived from the plot of a against the term $\log_{10}\frac{a^2}{(1-a)}$ fig.(28).

For example

$T^{o}K$	800	840	880	920	960
$(LogK_p - LogRT)$	-6.397	-5.928	-5.508	-5.118	-4.766
$Log_{10}(C=10^{-6})$	-6	-6	-6	-6	-6
$Log_{10}\ a^2/(1-a)$	-0.397	0.072	0.492	0.882	1.234
a	0.465	0.64	0.80	0.895	0.950

A plot of Log c versus a is given in fig.(29) showing the trend in dissociation with temperature and concentration.

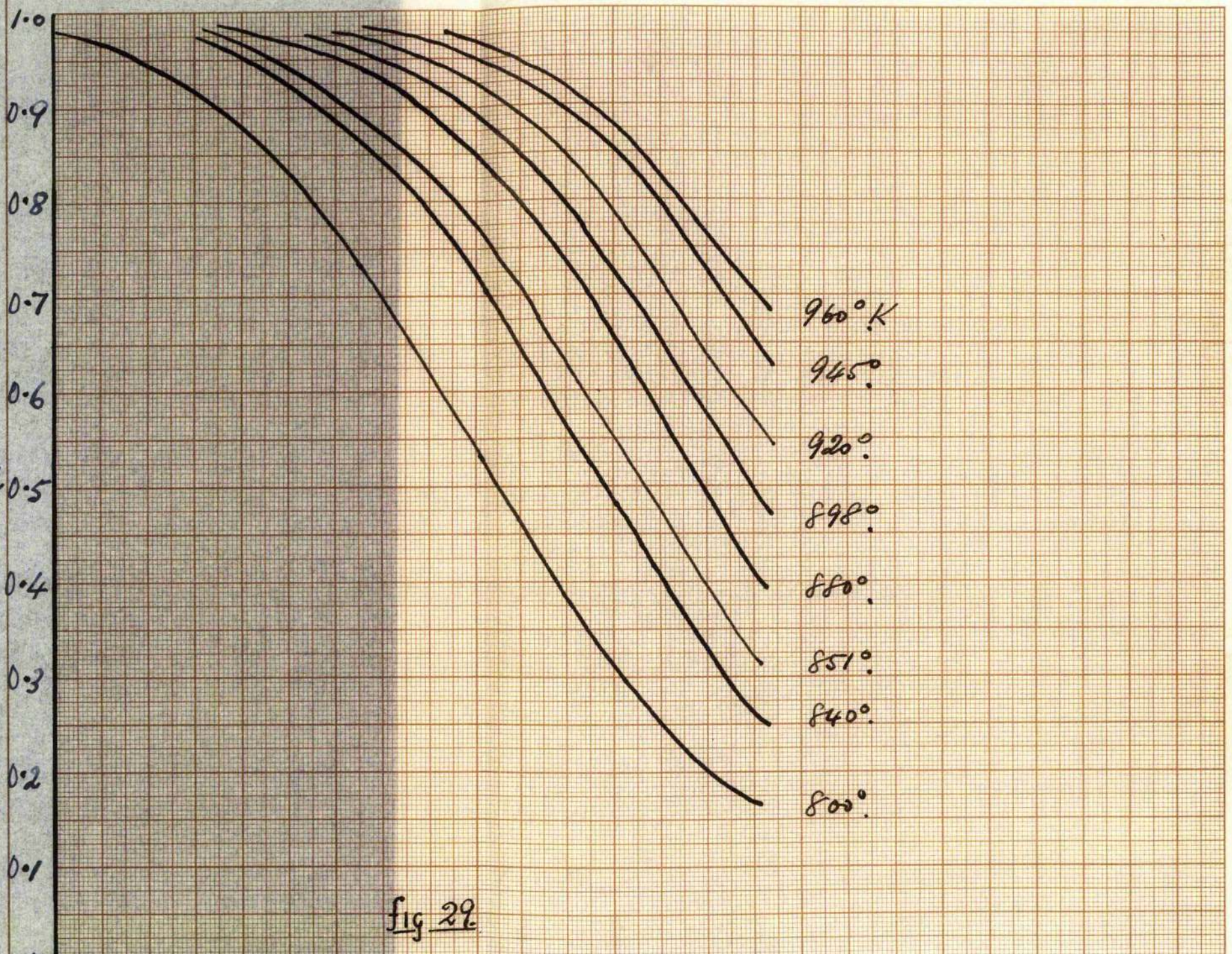


fig 29

Appendix (7)

Calculation of the decomposition of Hydrogen Iodide at 945°K.

According to Bodenstein [93]

$$2HI \longrightarrow H_2 + I_2$$

$$k_f = 10^{0.73} = 5.35 \text{ mole}^{-1} \text{ litre sec}^{-1} \quad \text{at } 945^\circ K.$$

If the concentrations used in the experiments with hydrogen iodide were approximately 5×10^{-7} moles/litre we have

$$\frac{dI_2}{dt} = 5.35 \ (5 \times 10^{-7})(5 \times 10^{-7}).$$

$$= 1.34 \times 10^{-12} \text{ moles/litre, sec.}$$

Therefore the quantity of iodine formed by the decomposition of hydrogen iodide at 945°K would be negligible in comparison to the observed rates of iodine formation in the reaction between dibenzyl and hydrogen iodide.

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Collective Table of Results.

All concentration units in moles X 10^{-7}/ litre unless otherwise indicated. L = large furnace ratio = 2.23 cm^{-1}. S = small furnace ratio = 12.25 cm^{-1}.

a. The Dissociation of Dibenzyl in the presence of Hydrogen Iodide.

Run No.	$T^{o}K$	$\frac{I_o}{T^{o}K} \times 10^{3}$	C.T. Sec.	(D.B.) Input.	(HI.) Exit.	(I_2) Exit.	(St.) Exit.	S/V.	PN_2 mm.	K_4 $Sec.^{-1}$
316	945	1.058	0.256	1.88	-	-	-	-	-	-
317	945	1.058	0.256	1.88	0.14	1.63	0.165	L	3.45	8.33
318	945	1.058	0.256	1.88	0.90	1.42	0.165	L	3.45	6.50
319	809	1.236	0.310	2.28	5.34	0.136	0.0	L	3.25	0.199
320	809	1.236	0.310	2.28	6.54	0.088	0.0	L	3.25	0.126
321	809	1.236	0.310	-	-	-	-	-	-	-
322	898	1.113	0.263	1.97	2.9	0.943	0.233	L	3.73	3.29
323	898	1.113	0.263	1.97	2.43	0.943	0.233	L	3.73	3.29
324	-	-	-	-	-	-	-	-	-	-
325	945	1.058	0.270	1.90	0.99	1.57	0.199	L	3.25	7.16
326	945	1.058	0.270	1.90	1.17	1.61	0.199	L	3.25	7.29
327	-	-	-	-	-	-	-	-	-	-
328	851	1.175	0.310	2.57	6.00	0.315	0.066	L	3.91	0.430
329	851	1.175	0.310	2.57	6.78	0.315	0.066	L	3.91	0.383
330	-	-	-	-	-	-	-	-	-	-
331	898	1.113	0.298	2.08	0.606	0.854	0.148	L	3.34	2.22
332	898	1.113	0.298	2.08	0.79	0.776	0.148	L	3.34	2.00
333	898	1.113	0.298	2.08	0.84	0.803	0.148	L	3.34	1.97
334	898	1.113	0.298	2.02	0.772	0.779	0.236	L	3.79	2.44
335	898	1.113	0.298	2.02	0.87	0.779	0.236	L	3.79	2.44
336	898	1.113	0.298	2.02	0.86	0.779	0.236	L	3.79	2.44
337	898	1.113	0.297	2.09	0.512	0.862	0.233	L	3.74	2.46
338	898	1.113	0.297	2.09	2.45	0.862	0.233	L	3.74	2.46
339	898	1.113	0.297	2.09	2.94	0.844	0.233	L	3.74	2.42
340	898	1.113	0.274	2.73	0.144	0.956	0.302	L	3.81	2.34
341	898	1.113	0.274	2.73	1.06	0.956	0.302	L	3.81	2.52
342	898	1.113	0.274	2.73	2.08	1.037	0.302	L	3.81	2.56
343	832	1.201	0.292	4.22	3.16	0.225	0.086	L	3.75	0.264
344	832	1.201	0.292	4.22	3.99	0.197	0.086	L	3.75	0.239
345	832	1.201	0.292	4.22	4.19	0.197	0.086	L	3.75	0.239

Run No.	$T^{o}K$	$\frac{I}{T^{o}K} \times 10^{3}$	C.T. Sec.	(D.B.) Input.	(HI.) Exit.	(I_2) Exit.	(St.) Exit.	S/V.	PN_2 mm.	K_4 $Sec.^{-1}$
346	874	1.144	0.274	3.96	3.82	0.713	0.323	L	3.77	1.051
347	874	1.146	0.274	3.96	3.65	0.713	0.323	L	3.77	1.051
348	874	1.144	0.274	3.96	3.90	0.713	0.323	L	3.77	1.056
349	-	-	-	-	-	-	-	-	-	-
350	921	1.085	0.268	1.29	1.24	1.12	0.135	L	3.73	7.77
351	921	1.085	0.268	1.29	1.5	1.05	0.135	L	3.73	6.87
352	921	1.085	0.268	1.29	1.6	1.05	0.135	L	3.73	6.87
353	898	1.113	0.256	4.53	5.4	1.50	0.472	L	3.83	2.23
354	898	1.113	0.256	4.53	5.29	1.50	0.472	L	3.83	2.32
355	898	1.113	0.256	4.53	5.0	1.50	0.472	L	3.83	2.32
356	813	1.230	0.288	5.04	-	0.140	0.01	L	3.83	0.1054
357	813	1.230	0.288	5.04	2.68	0.106	0.01	L	3.83	0.081
358	813	1.230	0.288	5.04	3.1	0.140	0.01	L	3.83	0.1054
359	945	1.057	0.241	1.55	4.5	1.31	0.154	L	3.83	10.06
360	945	1.057	0.261	1.55	5.1	1.22	0.154	L	3.83	7.46
361	945	1.057	0.261	1.55	-	-	-	-	-	-
362	898	1.113	0.268	7.84	9.4	2.12	1.13	L	3.95	1.98
363	898	1.113	0.268	7.84	17.0	2.03	1.13	L	3.95	1.98
364	898	1.113	0.268	7.84	-	-	-	-	-	-
383	898	1.113	0.464	4.81	1.6	1.21	0.501	L	3.82	1.035
384	898	1.113	0.464	4.81	2.0	1.19	0.501	L	3.82	0.978
385	898	1.113	0.464	4.81	2.3	1.17	0.501	L	3.82	0.964
386	898	1.113	0.329	3.39	2.07	0.872	0.283	L	3.82	1.15
387	898	1.113	0.329	3.39	2.07	0.827	0.283	L	3.82	1.10
388	898	1.113	0.329	3.39	2.07	0.872	0.283	L	3.82	1.15
389	898	1.113	0.916	9.42	5.6	1.91	1.84	L	3.84	0.55
390	898	1.113	0.916	9.42	6.3	1.91	1.84	L	3.84	0.55
391	-	-	-	-	-	-	-	-	-	-
392	898	1.113	0.262	1.57	2.0	0.761	0.116	L	7.41	3.09
393	898	1.113	0.262	1.57	2.0	0.725	0.116	L	7.41	2.93
394	898	1.113	0.262	1.57	2.0	0.761	0.116	L	7.41	3.09
395	898	1.113	0.278	3.99	0.37	1.11	0.500	L	7.35	1.97
396	898	1.113	0.264	3.78	0.49	1.14	0.476	L	7.35	2.08
397	898	1.113	0.264	3.78	0.52	1.13	0.476	L	7.35	2.06
398	898	1.113	0.180	2.25	2.0	0.858	0.136	L	7.38	3.28
399	898	1.113	0.180	2.25	2.0	0.799	0.136	L	7.38	3.03
400	898	1.113	0.180	2.25	2.0	0.832	0.136	L	7.38	3.17
401	898	1.113	0.098	16.56	7.9	1.94	0.727	S	7.83	1.85
402	898	1.113	0.098	16.56	7.9	1.95	0.727	S	7.83	1.84
403	898	1.113	0.098	16.56	7.9	1.94	0.727	S	7.83	1.85
404	898	1.113	0.068	7.96	6.8	0.96	0.142	S	12.7	2.20
405	898	1.113	0.068	7.96	6.8	0.97	0.142	S	12.7	2.22
406	898	1.113	0.068	7.96	6.8	0.97	0.142	S	12.7	2.22
407	898	1.113	0.068	3.65	8.0	0.605	0.0	S	12.7	2.68

Run No.	$T^{o}K$	$\frac{I}{T^{o}K} \times 10^{3}$	C.T. Sec.	(D.B.) Input.	(HI.) Exit.	(I_2) Exit.	(St.) Exit.	S/V.	PN_2 mm.	K_4 $Sec.^{-1}$
408	898	1.113	0.068	3.65	8.0	0.503	0.0	S	12.7	2.36
409	898	1.113	0.068	3.65	8.0	0.544	0.0	S	12.7	2.59
410	874	1.144	0.071	3.70	6.6	0.20	0.0	S	12.8	0.780
411	874	1.144	0.071	3.70	6.6	0.20	0.0	S	12.8	0.780
412	874	1.144	0.071	3.70	6.6	0.173	0.0	S	12.8	0.674
413	874	1.144	0.073	8.35	7.2	0.399	0.0	S	12.8	0.671
414	874	1.144	0.073	8.35	7.2	0.410	0.0	S	12.8	0.693
415	874	1.144	0.073	-	-	-	-	-	-	-
421	898	1.113	0.070	1.09	5.8	0.131	0.0	S	13.08	1.83
422	898	1.113	0.070	1.09	5.8	0.146	0.0	S	13.08	2.06
423	898	1.113	0.070	1.09	5.8	0.146	0.0	S	13.08	2.06
424	897	1.115	0.10	8.57	6.1	1.11	0.196	S	7.79	1.67
425	897	1.115	0.10	8.57	6.1	0.92	0.196	S	7.79	1.41
426	897	1.115	0.10	8.57	6.1	0.92	0.196	S	7.79	1.41
427	898	1.113	0.115	15.3	4.4	2.16	1.20	S	10.27	2.20
428	898	1.113	0.115	15.3	4.4	2.00	1.20	S	10.27	2.12
429	898	1.113	0.115	15.3	4.4	1.97	1.20	S	10.27	2.09
431	898	1.113	0.137	13.17	8.1	1.15	0.77	S	9.61	1.68
432	898	1.113	0.137	13.17	8.1	1.15	0.77	S	9.61	1.69
433	898	1.113	0.137	13.17	8.1	1.15	0.77	S	9.61	1.68
437	898	1.113	0.113	8.03	4.2	1.20	0.198	S	6.88	1.72
438	898	1.113	0.113	8.03	4.2	1.15	0.198	S	6.88	1.64
439	898	1.113	0.113	8.03	4.2	1.20	0.198	S	6.88	1.72
440	851	1.175	0.112	7.86	3.8	0.213	0.023	S	6.73	0.238
441	851	1.175	0.112	7.86	3.8	0.217	0.023	S	6.73	0.268
442	851	1.175	0.112	7.86	3.8	0.213	0.023	S	6.75	0.238
443	851	1.175	0.16	4.60	5.9	0.226	0.036	L	10.70	0.367
444	851	1.175	0.16	4.60	5.9	0.230	0.036	L	10.70	0.367
445	851	1.175	0.16	4.60	5.9	0.226	0.036	L	10.70	0.367
446	851	1.175	0.307	3.64	-	0.312	0.114	L	3.77	0.401
447	851	1.175	0.307	3.64	-	0.312	0.114	L	3.77	0.401
448	851	1.175	0.307	3.64	-	-	-	-	-	-
449	851	1.175	0.312	1.71	0.68	0.209	0.065	L	3.65	0.570
450	851	1.175	0.312	1.71	0.68	0.179	0.065	L	3.65	0.500
451	851	1.175	0.312	1.71	0.68	0.209	0.065	L	3.65	0.570
452	851	1.175	0.307	6.11	2.0	0.363	0.332	L	3.77	0.406
453	851	1.175	0.307	6.11	2.0	0.396	0.334	L	3.77	0.424
454	851	1.175	0.307	6.11	-	-	-	-	-	-
455	851	1.175	0.307	8.93	2.0	0.490	0.526	L	3.81	0.408
456	851	1.175	0.307	8.93	2.0	0.497	0.526	L	3.81	0.408
457	851	1.175	0.307	8.93	2.0	0.497	0.526	L	3.81	0.406
458	851	1.175	0.823	12.12	9.3	0.810	2.33	L	3.77	0.405
459	851	1.175	0.823	12.12	9.3	0.839	2.33	L	3.77	0.410
460	851	1.175	0.823	12.12	9.3	0.839	2.33	L	3.77	0.410
461	851	1.175	0.289	3.45	2.1	0.308	0.171	L	3.82	0.530
462	851	1.175	0.289	3.45	2.1	0.251	0.171	L	3.82	0.464
463	851	1.175	0.289	3.45	2.1	0.185	0.171	L	3.82	0.387

Run No.	T°K	$\frac{I}{T^{\circ}K} \times 10^{3}$	C.T. Sec.	(D.B.) Input.	(HI.) Exit.	(I_2) Exit.	(St.) Exit.	S/V.	PN_2 mm.	K_4 $sec.^{-1}$
464	851	1.175	0.289	5.78	3.23	0.398	0.229	L	3.82	0.393
465	851	1.175	0.289	5.78	3.23	0.400	0.229	L	3.82	0.403
466	851	1.175	0.289	5.78	3.23	0.400	0.229	L	3.82	0.403
467	851	1.175	0.306	2.95	1.5	0.252	0.064	L	3.87	0.373
468	851	1.175	0.306	2.95	1.5	0.268	0.064	L	3.87	0.407
469	851	1.175	0.306	2.95	1.5	0.268	0.064	L	3.87	0.407
470	851	1.175	0.307	1.67	2.34	0.168	0.025	L	3.77	0.401
471	851	1.175	0.307	1.67	2.34	0.168	0.025	L	3.77	0.401
472	851	1.175	0.307	1.67	2.34	0.168	0.025	L	3.77	0.401
473	851	1.175	0.467	2.54	-	0.307	0.079	L	3.91	0.358
474	851	1.175	0.467	2.54	-	0.300	0.079	L	3.91	0.355
475	851	1.175	0.467	2.54	-	0.300	0.079	L	3.91	0.355
476	809	1.236	0.337	4.04	8.0	0.066	0.0	L	3.89	0.0486
477	809	1.236	0.337	4.04	8.0	0.073	0.0	L	3.89	0.0537
478	809	1.236	0.337	4.04	-	-	-	-	-	-
479	809	1.236	0.320	4.69	6.8	0.10	0.0	L	3.77	0.0637
480	809	1.236	0.320	4.69	6.8	0.075	0.0	L	3.77	0.050
481	809	1.236	0.320	4.69	-	-	-	-	-	-
482	830.5	1.204	0.312	6.31	9.9	0.236	0.276	L	3.77	0.169
483	830.5	1.204	0.312	6.31	9.9	0.225	0.266	L	3.77	0.163
484	830.5	1.204	0.312	6.31	-	-	-	-	-	-
485	874	1.144	0.296	5.72	2.0	0.869	0.618	L	3.77	1.019
486	874	1.144	0.296	5.72	2.0	0.878	0.618	L	3.77	1.026
487	874	1.144	0.296	5.72	-	-	-	-	-	-
490	898	1.113	0.287	0.981	3.9	0.505	0.056	L	3.77	2.91
491	898	1.113	0.287	0.981	3.9	0.491	0.056	L	3.77	2.79
492	898	1.113	0.287	0.981	3.9	0.505	0.056	L	3.77	2.91

In addition hydrogen analyses were carried out and these results are listed below.

Run No.	(H_2)	Run No.	(H_2)
317	0.22	322	0.22
318	0.22	323	0.22
319	0.007	325	0.21
320	0.007	326	0.21

(b) Reaction between Dibenzyl and Iodine.

All results obtained in large furnace.

Run No.	$T^{\circ}K$	$I/T \times 10^3$	C.T. secs.	(D.B.) IN	(I_2) IN	(I_2) Mean	(St.) Exit	(HI.) Exit	$2\alpha I_2$ Mean	α	PN_2 mm.	$K_5 \times 10^{-7}$ mole $^{-1}$ litre sec $^{-1}$
286	945	1.059	0.236	2.04	9.0	8.57	1.62	1.73	16.1	0.94	3.83	-
287	945	1.059	0.236	2.04	9.42	8.97	1.62	1.72	16.8	0.94	3.83	-
288	945	1.059	0.236	2.04	9.47	9.08	1.62	1.54	16.9	0.94	3.83	-
289	898	1.113	0.246	11.09	9.0	7.5	4.84	6.02	13.1	0.88	3.60	0.23
290	898	1.113	0.246	11.09	9.37	7.5	4.84	6.58	13.1	0.88	3.60	0.23
291	898	1.113	0.246	11.09	9.36	7.57	4.84	7.17	13.2	0.88	3.60	0.23
292	810	1.235	0.280	3.90	11.72	11.42	1.99	1.86	10.9	0.49	3.61	0.24
293	810	1.235	0.280	3.90	12.1	11.60	1.99	1.95	11.1	0.49	3.61	0.24
294	810	1.235	0.280	3.90	12.1	11.90	1.99	2.06	11.3	0.49	3.61	0.24
295	851	1.175	0.267	2.63	12.1	11.90	1.06	0.81	15.7	0.66	3.76	0.14
296	851	1.175	0.267	2.63	12.24	12.04	1.06	0.80	15.9	0.66	3.76	0.14
297	851	1.175	0.267	2.63	12.37	12.15	1.06	0.87	16.0	0.66	3.76	0.13
301	945	1.059	0.247	11.34	9.66	8.95	7.55	2.82	16.8	0.94	3.80	-
302	945	1.059	0.247	11.34	9.91	9.21	7.55	3.00	17.2	0.94	3.80	-
303	945	1.059	0.247	11.34	10.06	9.34	7.55	3.08	17.5	0.94	3.80	-
365	898	1.113	0.258	1.29	9.81	9.41	1.11	1.55	16.2	0.86	3.91	0.40
366	898	1.113	0.258	1.29	9.43	9.16	1.11	1.25	15.8	0.86	3.91	0.47
367	898	1.113	0.258	1.29	8.93	8.63	1.11	1.17	15.0	0.87	3.91	0.51
368	898	1.113	0.264	1.28	4.80	4.60	0.94	0.85	8.50	0.92	3.78	0.30
369	898	1.113	0.264	1.28	4.90	4.67	0.94	0.94	8.60	0.92	3.78	0.30
370	898	1.113	0.264	1.28	4.81	4.58	0.94	0.97	8.40	0.92	3.78	0.30
371	898	1.113	0.262	3.64	3.87	3.50	2.11	1.47	6.50	0.94	3.88	0.66
372	898	1.113	0.262	3.64	3.67	3.30	2.11	1.46	6.10	0.94	3.88	0.73
373	898	1.113	0.262	3.64	3.98	3.58	2.11	1.58	6.70	0.94	3.88	0.64
374	898	1.113	0.268	3.65	4.26	3.89	2.30	1.47	7.20	0.93	3.83	0.52
375	898	1.113	0.268	3.65	4.32	3.92	2.30	1.59	7.30	0.93	3.83	0.52
377	898	1.113	0.261	3.21	10.1	9.24	2.99	3.41	16.0	0.86	3.90	0.36
378	898	1.113	0.261	3.21	10.8	9.90	2.99	3.60	17.0	0.86	3.90	0.34
379	898	1.113	0.261	3.21	10.34	9.40	2.99	3.46	16.40	0.86	3.90	0.34

In addition a hydrogen analysis performed on runs 301 - 303 showed a total hydrogen concentration of 0.18×10^{-7} moles/litre.

(c) Reaction Between Toluene and Iodine.

All concentrations moles x 10^{-7} / litre. All runs completed in large furnace. a = fraction of iodine dissociated into atoms.

$$K_1 = (HI - 2\ St.) / C.T.(C_7H_8)(2aI_2) \text{ moles}^{-1} \text{ litre sec}^{-1}.$$

Run No.	T^oK	$1/T^oK \times 10^3$	C.T. sec.	Toluene IN	(I_2) IN	α	$(2\alpha I_2)$ IN	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
40	852	1.175	0.39	23.6	10.4	0.70	14.55	-	0.42	-	5.72	-
41	852	1.175	0.38	23.9	10.5	0.70	14.70	-	0.42	-	5.72	-
42	852	1.175	0.40	22.6	9.92	0.70	13.90	-	0.48	-	5.72	-
43	852	1.175	0.26	22.8	2.24	0.90	4.04	-	0.31	-	5.35	-
44	852	1.175	0.26	22.8	2.24	0.90	4.04	-	0.32	-	5.35	-
45	852	1.175	0.25	21.7	2.14	0.90	3.86	-	0.31	-	5.35	-
46	852	1.175	0.28	25.6	2.13	0.90	3.85	-	0.42	-	4.08	-
47	852	1.175	0.31	27.7	2.31	0.90	4.16	-	0.46	-	4.08	-
48	852	1.175	0.31	27.7	2.31	0.90	4.16	-	0.46	-	4.08	-
49	852	1.175	0.28	23.9	6.94	0.77	10.7	-	-.84	-	3.90	-
50	852	1.175	0.27	23.0	6.66	0.77	10.25	-	0.75	-	3.90	-
51	852	1.175	0.27	23.0	6.66	0.77	10.25	-	0.90	-	3.90	-
55	852	1.175	0.30	27.9	9.08	0.73	13.23	-	0.87	-	3.99	-
56	852	1.175	0.28	26.3	8.57	0.74	12.75	-	0.88	-	3.99	-
58	852	1.175	0.27	21.7	4.73	0.90	8.52	-	0.76	-	3.78	-
59	852	1.175	0.28	23.9	5.93	0.90	10.70	-	0.83	-	3.78	-
60	852	1.175	0.26	21.2	4.77	0.90	8.60	-	0.68	-	3.78	-
61	852	1.175	0.26	21.2	4.07	0.83	6.75	-	0.57	-	3.88	-
62	852	1.175	0.26	21.2	4.07	0.83	6.75	-	0.53	-	3.89	-
63	852	1.175	0.26	21.2	4.07	0.83	6.75	-	0.51	-	3.89	-
64	852	1.175	0.26	21.3	11.25	0.70	15.75	-	0.51	-	4.03	-
65	852	1.175	0.26	20.9	11.07	0.70	15.5	-	0.49	-	4.03	-
66	852	1.175	0.27	21.6	11.4	0.70	16.0	-	0.69	-	4.03	-
67	852	1.175	0.28	24.3	7.55	0.75	11.3	-	0.95	-	3.99	-
68	852	1.175	0.28	24.3	7.55	0.75	11.3	-	0.92	-	3.99	-
69	852	1.175	0.28	24.3	7.55	0.75	11.3	-	0.99	-	3.99	-
70	852	1.175	0.27	22.8	11.83	0.70	16.6	-	1.16	-	3.92	-
71	852	1.175	0.27	22.8	11.83	0.70	16.6	-	1.16	-	3.92	-
72	852	1.175	0.27	22.8	11.83	0.70	16.6	-	1.18	-	3.92	-
73	852	1.175	0.28	23.3	14.8	0.65	19.25	-	1.41	-	4.0	-
74	852	1.175	0.28	23.3	14.8	0.65	19.25	-	1.29	-	4.0	-
75	852	1.175	0.27	23.9	14.5	0.65	18.85	-	1.48	-	4.0	-
76	898	1.113	0.27	30.5	5.5	0.91	10.0	-	0.87	-	3.95	-
77	898	1.113	0.28	31.2	5.6	0.91	10.2	-	0.96	-	3.95	-
78	898	1.113	0.28	31.2	5.6	0.91	10.2	-	0.87	-	3.95	-

Run No.	$T^{\circ}K$	$1/T^{\circ}K \times 10^{3}$	C.T. sec.	Toluene IN	(I_o) IN	α	$(2\alpha I_2)$ IN	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
79	898	1.113	0.30	45.0	5.8	0.91	10.6		1.21	-	3.85	-
80	898	1.113	0.30	45.0	5.8	0.91	10.6	-	1.17	-	3.85	-
81	898	1.113	0.30	45.0	5.8	0.91	10.6	-	1.38	-	3.85	-
82	898	1.113	0.29	53.5	5.8	0.91	10.6	-	1.42	-	3.80	-
83	898	1.113	0.29	53.5	5.9	0.91	10.75	-	1.47	-	3.80	-
84	898	1.113	0.29	53.4	5.9	0.91	10.75	-	1.47	-	3.80	-
85	898	1.113	0.29	17.2	5.6	0.90	10.2	-	0.50	-	3.80	-
86	898	1.113	0.30	18.1	5.9	0.91	10.7	-	0.46	-	3.80	-
87	898	1.113	0.30	18.1	5.9	0.91	10.7	-	0.50	-	3.80	-
88	898	1.113	0.30	14.2	5.9	0.91	10.7	-	0.50	-	3.78	-
89	898	1.113	0.30	14.2	5.9	0.91	10.7	-	0.54	-	3.78	-
90	898	1.113	0.30	14.2	5.9	0.91	10.7	-	0.58	-	3.78	-
91	874	1.144	0.26	21.9	5.4	0.91	9.8	-	0.91	-	3.80	-
92	874	1.144	0.26	21.9	5.4	0.91	9.8	-	1.09	-	3.80	-
93	874	1.144	0.26	21.7	5.3	0.92	9.7	-	1.10	-	3.80	-
94	874	1.144	0.27	31.4	5.3	0.92	9.7	-	1.19	-	3.90	-
95	874	1.144	0.27	31.4	5.3	0.92	9.7	-	1.31	-	3.90	-
96	874	1.144	0.27	32.0	5.4	0.88	9.56	-	1.42	-	3.90	-
97	865	1.156	0.26	21.8	4.9	0.84	8.23	-	0.70	-	3.90	-
98	865	1.156	0.26	21.8	4.9	0.84	8.23	-	0.73	-	3.90	-
99	865	1.156	0.26	21.7	4.9	0.84	8.23	-	0.80	-	3.90	-
100	874	1.144	0.26	24.2	8.0	0.82	13.15	-	1.49	-	3.80	-
101	874	1.144	0.28	25.6	8.4	0.81	13.60	-	1.64	-	3.80	-
102	874	1.144	0.28	25.6	8.4	0.81	13.60	-	1.64	-	3.80	-
103	863	1.158	0.36	30.6	10.5	0.76	15.98	-	1.86	-	3.90	-
104	863	1.158	0.30	26.1	9.0	0.78	14.05	-	1.63	-	3.90	-
105	863	1.158	0.30	26.1	9.0	0.78	14.05	-	1.53	-	3.90	-
106	827	1.209	0.27	23.9	7.7	0.64	9.85	-	0.60	-	3.90	-
107	827	1.209	0.27	24.2	7.59	6.64	9.70	-	0.62	-	3.85	-
108	827	1.209	0.28	25.2	7.8	0.64	9.99	-	0.63	-	3.85	-
109	827	1.209	0.28	30.6	4.2	0.74	6.22	-	0.56	-	3.75	-
110	827	1.209	0.29	32.0	4.3	0.74	6.37	-	0.62	-	3.75	-
111	827	1.209	0.29	32.1	4.3	0.74	6.37	-	0.61	-	3.75	-
112	827	1.209	0.28	26.9	4.6	0.73	6.72	-	0.48	-	3.75	-
113	827	1.209	0.28	27.1	4.7	0.73	6.86	-	0.50	-	3.75	-
114	827	1.209	0.29	27.1	4.7	0.73	6.86	-	0.45	-	3.75	-
115	898	1.113	0.28	24.0	4.9	0.91	8.9	0.42	1.74	-	3.88	1.56
116	898	1.113	0.28	24.0	4.9	0.91	8.9	0.42	2.00	-	3.88	1.86
117	898	1.113	0.28	24.0	4.9	0.91	8.9	0.41	1.86	-	3.88	1.74
118	898	1.113	0.27	32.5	5.2	0.92	9.6	0.44	1.88	-	3.73	1.59
119	898	1.113	0.27	32.8	5.2	0.92	9.6	0.44	1.83	-	3.73	1.35
120	898	1.113	0.27	32.8	5.2	0.92	9.6	0.44	2.56	-	3.73	2.32
121	921	1.085	0.27	20.7	9.9	0.90	17.8	-	4.06	-	3.9	-
122	921	1.085	0.27	20.7	9.9	0.90	17.8	-	3.31	-	3.9	-
123	921	1.085	0.27	20.7	9.9	0.90	17.8	-	3.58	-	3.9	-
124	945	1.058	0.26	23.1	7.0	0.96	13.5	0.35	2.65	-	3.9	3.15

Run No.	$T^{\circ}K$	$1/T^{\circ}K \times 10^{3}$	C.T. sec.	Toluene IN	(I_2) IN	α	$(2\alpha I_2)$ IN^2	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
125	945	1.058	0.26	23.1	7.02	0.96	13.4	0.35	2.71	-	3.90	3.2
126	945	1.058	0.26	23.0	7.02	0.96	13.4	0.35	2.71	-	3.90	3.3
130	944	1.059	0.24	23.7	6.6	0.96	12.6	0.56	3.63	0.15	3.90	4.42
131	944	1.059	0.24	23.7	6.6	0.96	12.6	0.56	3.42	0.15	3.90	3.98
132	944	1.059	0.24	23.7	6.6	0.96	12.6	0.56	3.20	0.15	3.90	3.61
133	921	1.085	0.25	16.9	7.9	0.93	14.8	0.32	2.24	0.33	3.78	3.40
134	921	1.085	0.25	16.9	7.9	0.93	14.8	0.32	2.15	0.33	3.78	3.65
135	921	1.085	0.25	16.9	7.9	0.93	14.8	0.32	2.33	0.33	3.78	3.60
139	934	1.071	0.31	29.4	7.9	0.94	14.8	0.84	3.58	-	3.96	1.61
140	934	1.071	0.31	29.4	9.8	0.92	17.72	0.84	4.29	-	3.96	1.86
141	934	1.071	0.31	29.4	12.9	0.89	23.0	0.84	4.58	-	3.96	1.42
145	933	1.071	0.25	19.9	5.3	0.95	10.0	-	1.75	-	3.90	-
146	933	1.071	0.25	19.9	5.3	0.95	10.0	-	1.92	-	3.90	-
147	933	1.071	0.25	19.9	5.4	0.95	10.0	-	1.87	-	3.90	-
148	898	1.113	0.26	22.9	10.5	0.85	17.8	-	1.32	-	3.82	-
149	898	1.113	0.25	21.7	10.0	0.85	17.0	-	1.65	-	3.82	-
150	898	1.113	0.26	22.9	10.5	0.85	17.8	-	1.69	-	3.82	-
151	921	1.085	0.26	26.1	6.9	0.94	13.0	-	2.00	-	3.82	-
152	921	1.085	0.26	26.1	6.9	0.94	13.0	-	2.75	-	3.82	-
153	921	1.085	0.26	26.1	7.8	0.92	14.4	-	3.26	-	3.82	-
154	939	1.064	0.25	26.1	9.8	0.93	18.2	0.80	3.40	0.33	3.74	1.62
155	939	1.064	0.25	27.4	9.8	0.93	18.2	0.80	3.14	0.33	3.74	1.38
156	939	1.064	0.25	27.4	9.8	0.93	18.2	0.80	3.34	0.33	3.74	1.60
158	927	1.078	0.25	27.4	8.4	0.92	15.4	0.69	2.59	0.17	3.68	1.54
159	927	1.078	0.25	22.2	8.5	0.92	15.8	0.69	2.73	0.17	3.68	1.69
160	921	1.085	0.26	22.5	9.3	0.90	16.8	0.55	2.45	0.17	3.77	1.30
161	921	1.085	0.26	26.4	7.3	0.92	13.46	0.55	2.62	0.05	3.77	1.30
162	921	1.085	0.26	26.4	7.61	0.92	14.0	0.55	3.03	0.06	3.77	2.25
163	914	1.094	0.26	27.5	12.18	0.87	19.6	0.73	3.58	0.12	3.84	1.53
164	914	1.094	0.26	28.8	12.2	0.87	19.6	0.73	3.76	0.12	3.84	1.67
165	914	1.094	0.26	28.8	12.2	0.87	19.6	0.73	3.83	0.12	3.84	1.72
166	939	1.064	0.24	41.8	9.0	0.94	16.8	1.25	5.78	0.52	3.85	2.43
167	939	1.064	0.24	41.8	9.0	0.94	16.8	1.25	5.82	0.59	3.85	2.65
168	939	1.064	0.24	41.8	9.0	0.94	16.8	1.25	5.34	0.59	3.85	2.06
169	939	1.064	0.25	37.3	9.9	0.93	18.4	1.11	5.27	0.54	3.87	2.10
170	939	1.064	0.25	37.3	9.9	0.93	18.4	1.11	5.28	0.54	3.87	2.10
171	939	1.064	0.26	37.9	10.1	0.93	18.7	1.11	5.45	0.54	3.87	2.15
172	910	1.098	0.26	36.4	10.1	0.88	17.8	0.64	3.92	-	3.82	1.84
173	910	1.098	0.25	37.0	10.3	0.88	18.1	0.64	3.66	-	3.82	1.58
174	910	1.098	0.25	36.9	10.2	0.88	18.0	0.64	3.64	-	3.82	1.59
175	868	1.152	0.27	39.3	10.7	0.78	16.9	0.41	2.97	0.16	3.93	1.56
176	868	1.152	0.27	39.3	10.7	0.78	16.9	0.41	2.70	0.16	3.93	1.36
177	868	1.152	0.27	39.3	10.7	0.78	16.9	0.41	2.45	0.16	3.93	1.13
178	881	1.135	0.29	44.5	12.3	0.78	19.2	0.55	2.96	-	3.90	0.87
179	881	1.135	0.28	42.4	15.0	0.75	23.4	0.55	3.37	-	3.90	0.96
180	881	1.135	0.28	42.4	12.6	0.78	20.0	0.55	3.02	-	3.90	0.73

Run No.	$T^{\circ}K$	$1/T^{\circ}K \times 10^3$	C.T. sec.	Toluene IN	(I_2) IN	α	$(2\alpha I_2)$ IN	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
181	892	1.121	0.27	38.7	8.7	0.86	15.0	0.61	3.61	-	3.88	1.60
182	892	1.121	0.27	39.3	8.9	0.87	15.4	0.61	3.14	-	3.88	1.49
183	892	1.121	0.27	39.3	8.9	0.84	15.0	0.61	3.38	-	3.88	1.36
184	944	1.059	0.25	37.7	9.7	0.94	18.4	0.85	4.95	0.14	3.92	2.25
185	944	1.059	0.25	37.7	9.7	0.94	18.4	0.85	4.88	0.14	3.92	2.23
186	944	1.059	0.25	37.4	9.6	0.94	18.0	0.85	4.35	0.14	3.92	2.00
187	969	1.032	0.24	34.3	10.6	0.97	20.5	1.03	5.02	0.10	3.83	2.45
188	969	1.032	0.24	34.3	10.9	0.97	21.1	1.03	5.69	0.10	3.83	2.69
189	969	1.032	0.24	35.0	10.9	0.97	21.1	1.03	5.75	0.10	3.83	2.76
190	945	1.058	0.35	51.8	12.7	0.92	23.5	2.07	8.57	0.14	3.99	1.12
191	945	1.058	0.35	51.8	12.7	0.93	23.5	2.07	8.67	0.14	3.99	1.28
192	945	1.058	0.35	51.8	12.7	0.93	23.5	2.07	7.64	0.14	3.99	1.03
193	957	1.044	0.24	34.7	7.8	0.96	14.9	0.91	3.9	0.14	3.94	1.94
194	957	1.044	0.24	34.1	7.8	0.96	14.9	0.91	4.58	0.14	3.94	2.49
195	957	1.044	0.24	34.1	7.8	0.96	14.9	0.91	4.42	0.14	3.94	2.49
196	963	1.040	0.22	32.3	5.7	0.98	11.2	0.67	3.03	0.15	3.84	2.46
197	963	1.040	0.23	32.8	5.2	0.98	10.0	0.67	2.84	0.15	3.84	2.36
198	963	1.040	0.23	32.8	5.2	0.98	10.0	0.67	2.72	0.15	3.84	2.26
199	951	1.051	0.23	34.2	10.1	0.98	19.5	0.98	4.40	0.30	3.90	1.99
200	951	1.051	0.23	34.2	10.1	0.97	19.5	0.98	4.03	0.30	3.90	1.62
201	951	1.051	0.23	32.7	9.7	0.97	18.8	0.98	4.98	0.30	3.90	2.62
202	898	1.113	0.25	36.2	10.7	0.83	17.9	0.79	4.15	0.11	3.84	1.55
203	898	1.113	0.25	36.2	10.7	0.85	17.9	0.79	3.73	0.11	3.84	1.35
204	898	1.113	0.24	35.0	10.3	0.87	17.9	0.79	3.27	0.11	3.84	1.19
205	827	1.209	0.27	38.0	8.4	0.65	10.6	0.10	1.06	-	3.93	0.83
206	827	1.209	0.27	38.0	8.4	0.64	10.6	0.10	1.13	-	3.93	0.94
207	827	1.209	0.27	38.0	8.4	0.64	10.6	0.10	1.13	-	3.93	0.94
208	841	1.189	0.27	40.7	9.74	0.64	12.5	0.12	1.46	-	3.84	0.93
209	841	1.189	0.25	37.6	9.0	0.66	11.9	0.12	1.39	-	3.84	1.58
210	841	1.189	0.25	37.6	10.3	0.64	13.1	0.12	1.65	-	3.84	1.18
211	851	1.175	0.28	40.1	8.96	0.72	13.0	0.17	1.91	0.02	3.82	1.15
212	851	1.175	0.28	40.4	8.2	0.74	12.2	0.17	1.62	0.02	3.82	1.17
213	851	1.175	0.28	40.4	8.2	0.76	12.4	0.17	1.61	0.02	3.82	1.24
214	862	1.160	0.27	39.5	13.1	0.73	19.2	0.20	1.99	0.02	3.92	1.10
215	862	1.160	0.27	39.5	9.6	0.75	14.5	0.20	1.74	0.02	3.92	1.03
216	862	1.160	0.27	39.5	9.8	0.75	14.8	0.20	1.86	0.02	3.92	1.13
217	809	1.235	0.28	39.0	6.9	0.58	8.1	0.01	0.73	-	3.87	0.86
218	809	1.235	0.27	38.0	7.1	0.58	8.4	0.01	0.79	-	3.87	0.96
220	816	1.225	0.27	38.5	10.5	0.54	11.2	0.02	1.18	-	3.82	0.90
221	816	1.225	0.26	35.6	10.9	0.54	11.7	0.02	1.14	-	3.92	0.95
223	946	1.055	0.28	33.0	5.92	0.96	11.3	5.36	3.74	-	3.88	2.85

Run No.	$T^{\circ}K$	$1/T^{\circ}K \times 10^{3}$	C.T. sec.	Toluene IN	(I_2) IN	α	$(2\alpha I_2)$ IN	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
224	946	1.057	0.25	30.8	6.4	0.96	12.3	0.54	3.36	-	3.88	3.15
225	946	1.057	0.25	30.8	6.4	0.96	12.3	0.54	3.45	-	3.88	3.28
226	945	1.058	0.22	26.3	34.2	0.97	56.0	1.65	7.96	-	3.77	1.69
228	945	1.058	0.22	26.3	40.5	0.82	61.6	1.65	9.27	-	3.77	1.92
229	945	1.058	0.23	27.6	22.7	0.76	39.4	1.52	7.66	-	4.04	2.33
230	945	1.058	0.23	27.6	22.7	0.87	39.4	1.52	7.37	-	4.04	2.29
231	945	1.058	0.23	27.6	22.7	0.87	39.4	1.52	7.32	-	4.04	2.28
232	945	1.058	0.22	28.4	14.5	0.87	26.4	1.06	5.87	-	3.87	2.98
233	945	1.058	0.22	28.4	14.6	0.91	26.6	1.06	5.73	-	3.87	2.80
234	945	1.058	0.22	28.4	14.2	0.91	26.0	1.06	5.50	-	3.87	2.69
235	945	1.058	0.23	16.5	7.6	0.91	14.4	0.44	2.61	-	3.92	4.15
236	945	1.058	0.23	16.5	7.4	0.95	14.0	0.44	2.55	-	3.92	3.93
237	945	1.058	0.23	16.5	7.4	0.95	14.0	0.44	2.70	-	3.92	4.38
238	945	1.058	0.26	24.6	7.9	0.95	14.9	0.50	3.80	-	3.92	4.02
239	945	1.058	0.23	21.4	7.4	0.95	14.4	0.50	3.23	-	3.92	4.31
240	945	1.058	0.23	21.4	7.4	0.95	14.4	0.50	2.91	-	3.92	3.69
241	945	1.058	0.18	14.9	20.4	0.95	35.4	0.73	4.22	-	7.70	3.07
242	945	1.058	0.18	14.9	20.4	0.87	35.4	0.73	4.32	-	7.70	3.19
243	945	1.058	0.18	14.9	20.6	0.87	35.4	0.73	4.04	-	7.70	2.85
244	945	1.058	0.19	24.2	17.0	0.89	33.0	1.16	6.27	-	7.48	3.07
245	945	1.058	0.19	24.2	17.0	0.89	33.0	1.16	6.15	-	7.48	3.02
246	945	1.058	0.19	24.2	17.0	0.89	33.0	1.16	6.40	-	7.48	3.20
247	945	1.058	0.22	26.0	18.2	0.90	32.6	1.35	6.09	-	3.93	2.16
248	945	1.058	0.22	26.0	18.2	0.90	32.6	1.35	6.14	-	3.93	2.19
249	945	1.058	0.22	26.0	18.2	0.90	32.6	1.35	6.70	-	3.93	2.55
250	945	1.058	0.27	19.1	13.4	0.92	24.6	0.92	4.24	-	2.60	2.23
251	945	1.058	0.27	19.1	13.4	0.92	24.6	0.92	4.44	-	2.60	2.43
252	945	1.058	0.27	19.1	13.4	0.92	24.6	0.92	4.41	-	2.60	2.40
253	945	1.058	0.18	28.6	17.5	0.90	31.6	-	5.77	-	7.85	-
254	945	1.058	0.18	28.6	17.5	0.90	31.6	-	5.79	-	7.85	-
255	945	1.058	0.18	-	-	-	-	-	-	-	-	-
256	945	1.058	0.25	35.6	21.7	0.88	38.2	1.62	7.81	-	5.08	1.60
257	945	1.058	0.25	35.6	21.7	0.88	38.2	1.62	7.75	-	5.08	1.60
258	945	1.058	0.25	35.6	21.7	0.88	38.2	1.62	7.57	-	5.08	1.50
259	945	1.058	0.19	27.0	34.1	0.83	56.3	2.26	10.80	-	7.39	2.65
260	945	1.058	0.19	27.3	34.4	0.83	56.8	2.26	10.04	-	7.39	2.24
261	945	1.058	0.19	27.3	34.4	0.83	56.8	2.26	10.63	-	7.39	2.61
262	945	1.058	0.24	12.3	14.2	0.91	25.8	0.59	3.37	-	3.82	3.36
263	945	1.058	0.24	12.3	13.4	0.91	24.4	0.59	3.44	-	3.82	3.72
264	945	1.058	0.24	12.3	12.2	0.91	22.2	0.59	3.25	-	3.82	3.62
265	945	1.058	0.23	7.03	19.9	0.89	35.2	0.43	2.76	-	3.71	3.95
266	945	1.058	0.23	7.03	19.4	0.89	34.4	0.43	2.75	-	3.71	4.14
267	945	1.058	0.23	7.03	18.8	0.89	33.2	0.43	2.91	-	3.71	4.62

Run No.	$T^{o}K$	$1/T^{o}K \times 10^{3}$	C.T. sec.	Toluene IN	(I_2) IN	α	$(2\alpha I_2)$ IN	(St.) Exit.	(HI.) Exit.	(H_2) Exit.	PN_2 mm.	$K_1 \times 10^{-5}$
268	945	1.058	0.23	4.46	18.5	0.89	32.8	0.27	1.90	-	3.78	5.00
269	945	1.058	0.23	4.46	18.5	0.89	32.8	0.27	1.96	-	3.78	5.25
270	945	1.058	0.23	4.46	18.5	0.89	32.8	0.27	2.07	-	3.78	5.75
271	945	1.058	0.23	4.08	17.2	0.90	31.0	0.15	1.97	-	3.83	-
272	945	1.058	0.23	3.95	16.6	0.90	30.0	0.15	3.54	-	3.83	-
274	945	1.058	0.23	22.9	20.5	0.88	36.0	1.38	6.17	-	3.97	2.39
275	945	1.058	0.23	22.9	20.5	0.88	36.0	1.38	5.85	-	3.99	2.19
276	945	1.058	0.23	22.9	20.5	0.88	36.0	1.38	6.41	-	3.99	2.58
277	945	1.058	0.23	37.6	22.7	0.88	40.0	1.85	9.38	-	3.79	2.09
278	945	1.058	0.23	37.6	22.7	0.88	40.0	1.85	9.12	-	3.79	2.00
279	945	1.058	0.23	37.6	22.7	0.88	40.0	1.85	9.17	-	3.79	2.01
280	945	1.058	0.23	40.9	21.2	0.90	38.4	1.29	8.91	-	3.74	-
281	945	1.058	0.22	40.1	20.8	0.90	37.4	1.29	10.80	-	3.94	-
283	945	1.058	0.23	19.8	11.7	0.93	21.8	0.39	4.04	-	3.91	-
284	945	1.058	0.23	19.0	12.2	0.93	22.7	0.39	6.89	-	3.91	-

Tests of Hydrogen Iodide inhibition.

Run No.	Hydrogen Iodide input moles $\times 10^{-7}$/litre.
272	2.56
281	4.04
284	5.35